ORIGIN OF NATURAL GAS IN SOUTH OF IRAN

A.R. Rabbani
Amirkabir University, Department of Petroleum Engineering, Tehran Iran

Abstract—Isotopic geochemical characteristics were determined in gases and condensates from southern Iran, which is one of the world's richest gas-bearing territories. The isotopic composition of methane and its homologues, the carbon isotope composition of CO₂, the chemical composition of gases, the isotopic composition of condensates, and the proportions of individual hydrocarbons in the condensates were analyzed. The analytical results demonstrated fairly uniform chemical compositions for gases and isotopic compositions of methane and its homologues in the section overlying the anhydrite zone. For instance, the values δ¹³C of methane in samples from this part of the section (Late Permian Dalan Formation, zone D,C,E and Early Triassic Kangan Formation) varied from -39.95 to -41.28‰. This allows us to conclude that gas accumulations in the carbonate collectors of the Kangan and upper part of Dalan formations represent a single gas reservoir. Quite different characteristics are displayed by gases from the lower zone (below the anhydrite) of the Dalan Formation (zone G). These gases are characterized by considerable depletion in the light carbon isotope. For instance, methane from the lower part of Dalan formation have δ¹³C = -26.22‰. They show also a number of other distinctive features: significant enrichment in nitrogen, occurrence of isotopically light CO₂ (δ¹³C = -21.87‰), and an inversion in the isotope relationships of ethane and propane. These peculiarities suggest that the composition of gases in this zone was modified by the process of the thermal chemical reduction of anhydrite. The isotopic compositions of condensates from the overlying and underlying the anhydrites zone are similar. The source of gases could be either the rocks of the Dalan Formation or Ordovician-Silurian shales. The formation of gas accompanied by condensate began when the Ordovician-Silurian rocks entered the stage of catagenesis corresponding to R₀ = 1.0-1.2%, which probably took place at the end of the Jurassic and beginning of the Cretaceous. The gas formation continued simultaneously with the burial of the sedimentary prism. Younger deposits including Permian ones entered the stage of gas generation. The Permian-Triassic collector was filled with gas. The subsequent portions of gas and condensate were accumulated in the lower part of the Paleozoic section. At that time, both the graptolite shales and anhydrites occurred at depths where the process of the thermal chemical reduction of sulfates exerted considerable influence on the composition of gases and organic matter. This resulted in the formation of the observed geochemical characteristics of gases in the lower zone, which are significantly different from the geochemical characteristics of gases from the upper zone.

Keyword: Iran, Dalan Gas Reservoir, Gas Origin, Isotope Geochemistry, Catagenesis

INTRODUCTION

The Upper Permian Dalan and Lower Triassic Kangan Formations contain extensive gas reservoirs in the south Iran and Persian Gulf area. In such gas fields as Kangan, Aghar, Nar, Pars and some others in Southern Iran more than 18 % of the proved gas reserves of the world are concentrated[1]. The Southern Pars field, which is one of the largest gas accumulations in the world, contains about 8.5×10¹² m³ of gas in the Dalan and Kangan gas reservoirs. In addition to the Southern Pars field, considerable volumes of Permian gas in Iran have been recovered in the Fars and Boshehr coastal provinces from the Kangan, Aghar, Nar, Varavi, Mond, Dalan, and Pars structures (Fig. 1). In the Persian Gulf shelf, the Permian section is penetrated by several boreholes drilled into the Pars (Iran), Idd al Sharji, Shajiah (United Arab Emirates), and Iminiko (Bahrain) structures. Gas pools have long been exploited in Bahrain and Saudi Arabia (Damman field), where they are confined to the Upper Permian section.

Gas accumulations related to the Permian sequences were first developed in Bahrain. Large gas pools are also known to exist in Saudi Arabia, Kuwait, and the United Arab Emirates. Thus, the zone of the Persian Gulf including southern Iran is one of the world's largest gas-bearing provinces. However the problems of gas origin in these territories are still open, and the geochemical characteristics of gases are poorly known.

The objectives of this paper are to:
(1) The characterization of the chemical and isotopic compositions of gases from southern Iran,
(2) Compare the composition of gases with source rock type and source rock thermal maturity, and
(3) Interpret the origin of gases.

GEOLOGICAL DESCRIPTION

In the Persian Gulf zone, the Permian gas reservoir is known as the Khuff Formation. This sequence is composed mainly of carbonate rocks and exists in Bahrain Qatar, Abu Dhabi, Saudi Arabia, and Iran.
The term Khuff Formation was coined by Bramkamp et al. [2] for an Upper Permian carbonate sequence, 564 ft (172 m) thick, which was described by them in Saudi Arabia. Since then, the term has widely been used by petroleum companies working in the Persian Gulf zone. Based on paleontological data, the upper part of the Khuff Formation (1100 m) was assigned in southern Iran to the Triassic [3]. In 1976, the Stratigraphic Committee of Iran renamed the Khuff Formation to Deh Ram Group [4] (Fig. 2). Three formations are distinguished in the Deh Ram Group: a lower Early Permian Faraghan Formation composed of terrigenous rocks; a middle Late Permian Dalan Formation composed of carbonate rocks and evaporite; and an upper Early Triassic Kangan Formation made up of massive carbonate rocks [5]. The Dalan formation comprise two large gas reservoirs in the lower (zone G) and in the upper portions (zones C and D), which are separated by a massive anhydrite bed in the middle part of the section.

Lithologically, the Deh Ram sequences of Iran are similar to the rocks of the Khuff Formation, which were comprehensively studied in the Persian Gulf zone. The latter are represented by a complex of dolomite, limestone, and anhydrite. Dolomite accounts for up to 75% of the rocks. The formation is 750-900 m thick. Khuff Formation was accumulated in a shallow marine basin environment [6]. The organic matter is described as predominantly humic with layers of material of the sapropel type. The content of organic matter ranges from 0.5-1.0%, the value Ro of vitrinite reflectance is 1.0-1.5%. The Dalan Formation is composed of biogenic limestone dolomitized to a large extent. It is represented by the reef and evaporite facies. The lower portion of the Dalan Formation is built up of a dark massive stratified in places by biogenic limestone and dolomite with an Oolitic structure. Carbonates from the upper part of the Dalan Formation and Lower Triassic sequences (Kangan Formation) are facially uniform.

In the middle part of the Dalan Formation, anhydrites show relatively high abundances of organic matter (1.7%). It is believed that the organic matter was deposited under conditions of relatively shallow, density stratified, waters with brine in the bottom zone. It was affected by significant microbiological transformation in the sediment [7].

The carbonate rocks show low porosity and permeability, but fracturing and dolomitization are ubiquitous in them [8]. Jointing and fracturing are well-developed in folded areas in thick sheets of carbonate rocks. Gas collectors are represented by thick dolomite sequences, porous pelletoid-oolite limestone, and less common layers of lumpy anhydrite. The main types of porosity are interoolitic, intergranular, and fissure. In the Kangan Formation, the porosity of rocks is mainly within 1-7% (5% on average). In the Dalan rocks, this parameter varies from 2 to 20% (10% on average). Permeability varies widely from less than one to a few tens of millidarcy. The Permian gas collectors are mainly overlain by impermeable layers.
However, in the southeast (in the Zagros geosyncline) and in the Persian Gulf (near northern Oman), the thick Permian carbonate sequence is overlain by Triassic carbonate sequences. The continuous Late Permian-Early Triassic carbonate section can be a single collector, especially in places where it is overlain by Triassic evaporite (lower portions of the Dashtak Formation), which forms efficient gas-impermeable horizons.

In the Silurian-Ordovician sediments (Gahkom Formation), there is a sequence more than 100 m thick of graptolite shales. Dark-colored shales contain from 1.0 to 4.3% of organic matter. The reconstruction of sedimentary history suggests that these deposits were buried at depths of 6000 m before their ascent to the modern level during the Zagros orogeny [9]. The organic matter of the graptolite shale is transformed almost to the state of graphitization. Some authors considered the Ordovician-Silurian deposits as a possible source of the giant gas accumulations in the Permian-Triassic deposits of the Khuff Formation in Iran, Qatar, and Abu Dhabi[10, 11].

**STUDY METHODS**

Gas composition was measured on a Tsvet-500 chromatograph. The volume concentrations of nitrogen (N2), carbon dioxide (CO2), methane (C1), ethane (C2), propane (C3), butane (C4), helium (He), and hydrogen sulfide (H2S) were determined.

The isotopic compositions of individual hydrocarbons were determined on a FINNIGAN MAT Delta Plus mass spectrometer with a preparative chromatographic system. Carbon dioxide was recovered preliminarily by introducing Ba(OH)2 into the gas sample. The resulting barium carbonate was precipitated and dried, and CO2 was then released using orthophosphoric acid and its carbon isotope composition was analyzed. The results of carbon isotopic analysis in hydrocarbons and CO2 are presented as δ13C relative to the PDB standard. The precision of analysis was within 0.2-0.3 ‰.

The pyrolysis parameters of organic matter were determined on a Rock Eval device. Free hydrocarbons were sublimated at a temperature of 300°C (peak S1). At temperatures from 300 to 600°C, bonded hydrocarbon structures (peak S2), which are responsible for the hydrocarbon capacity of the rock, were separated from kerogen and released. The discharge of S1 and S2 is measured in milligrams of hydrocarbons (HC) per one gram of rock. The temperature at which peak S2 attains a maximum (Tmax in °C) correlates with the degree of organic matter transformation. Oxygen-bearing compounds were decomposed at temperatures between 300 and 390°C and the resulting CO2 was manifested as peak S1, measured in mg CO2/g per rock. The complete oxidation of
organic carbon in combination with the carbon of pyrolysis products yields the value of the total organic carbon (TOC, wt %).

The burial history of sedimentary deposits of the geological section under question was reconstructed using the Jennex computer program.

The IR spectra of bitumen were recorded on a Specord IR-75 spectrometer having applied the concentrated solution of the material in chloroform onto KBr plates. The material film was carefully smoothed and kept until the complete elimination of chloroform. Bitumen extraction was performed in Soxhlet-type apparatuses with a benzene-methanol mixture (9:1) over 48 h. The extract was filtered and concentrated using a rotary evaporator. The purification of bitumen from elementary sulfur was carried out using activated copper.

The composition of condensate was determined on a Yanako G180-TFR gas chromatograph. The calculation and identification of components of organic matter were carried out on a CHROMOTOPAK C-R3A integrator.

RESULTS AND DISCUSSION

The results of the chemical and isotopic analysis of gases are shown in Table 1. The section of the Nar field was studied in the most detail. Gases from the Kangan Formation within the interval 1801-1983 m and from upper part of the Dalan Formation in the interval 2036-2328 m (zone D,E) show a striking similarity in chemical and isotopic characteristics. Methane content in the gas varied from 84.7 to 87.5% in five wells in the Kangan Formation. The isotopic compositions of gases were even more uniform: the δ\(^{13}\)C values measured varied from -40.26 to -40.61‰. Essentially identical geochemical characteristics were obtained for gases from the Dalan Formation (zone D,E): the methane content in eight wells varied between 84.4 and 87.6% and δ\(^{13}\)C, from -39.95 to -41.28‰. Similarly uniform isotopic composition was obtained for δ\(^{13}\)C of methane homologues: ethane (C\(_2\)) and propane (C\(_3\)). The δ\(^{13}\)C of these hydrocarbons from various intervals of the section of the Kangan Formation and zone D,E of the Dalan Formation varied within very narrow limits, δ\(^{13}\)C\(_2\) = -30.5 ± 0.5‰ and δ\(^{13}\)C\(_3\) = -29 ± 1‰.

The concentrations of CO\(_2\) and N\(_2\) in the gases were approximately equal. The isotopic composition of CO\(_2\) was also uniform, δ\(^{13}\)C varied from -10.51 to -15.51‰. These characteristics leave no doubt that the gas accumulations of the Kangan and Dalan (zone D,E) formations are related to a single gas reservoir.

Gases from the lower portion of the Dalan Formation (zone G) show fundamentally different characteristics. These gases are conspicuous in having a significant depletion in the light carbon isotope. For instance, methane from a pool occurring at a depth of 3600-3655 m in the Dalan Formation shows δ\(^{13}\)C = -26.22‰. This is consistent with a value of δ\(^{13}\)C = -23‰ reported previously for the deep horizons of the Khuff Formation in Abu Dhabi [12]. Two other gas samples from zone G showed δ\(^{13}\)C = -31.24 and -38.73‰ in the Trakome and Aggar.
fields, respectively. The carbon isotopic composition of methane homologues in the gas of zone G is also distinctive. In contrast to gases from the upper zone, the values $\delta^{13}C_2$ and $\delta^{13}C_3$ are significantly higher and their proportion is inverted: $\delta^{13}C_2 = -25.1 \pm 1.0\permil$ and $\delta^{13}C_3 = -26.2 \pm 0.5\permil$. These data suggest that the gas accumulations in zone G are related to a reservoir genetically different from the gas reservoir of the Early Triassic-Late Permian Formations (zone D,E) and are not so uniform as the latter. The gases of zone D are distinctive in a number of other geochemical parameters. They are significantly enriched in nitrogen. The nitrogen content in the isotopically heaviest gases is 35-38%. In contrast, their He content is very low (about 0.01%), i.e., nitrogen is probably of an exogenic origin.

Which Formation could be sources of gas in these gas reservoirs? It is well known that there is a correlation between the isotopic composition of gas (methane and its homologues) and the degree of transformation of initial gas-generating organic matter [13-22]. It has been empirically established that this relationship was different for sapropel and humus organic materials [15, 17, 23]. It has been demonstrated that this distinction is due to the fact that methane generation from a polymer substance of irregular structure (kerogen) is characterized by a certain band of activation energy, and that humus and sapropel organic matter differ in the distribution function of activation energy [19, 24, 25]. The carbon isotopic composition of methane homologues ($C_2$, $C_3$, and $C_4$) also has a bearing on the genesis of the hydrocarbon gas [26-30]. Proceeding from these regularities, methods of genetic gas identification were developed, which have also been used in this paper.

Empirical relationships were proposed for the dependence of gas isotopic composition on the degree of transformation of initial organic matter, i.e., dependencies of the type $\delta^{13}C_{CH_4} - R_o$, where $R$ is the vitrinite reflectance [15].

Vitrinite was not found by coal petrographers in the rock samples studied by us (L.I. Bogolyubova, personal communication). Because of this, we used an indirect method of $R_o$ estimation. Using the Rock Eval apparatus of our laboratory, we determined the values $T_{max}$ at the pyrolysis of organic matter. The parameter $T_{max}$ correlates with the degree of organic matter transformation. In the section under consideration, $T_{max}$ increases with increasing depth (Fig. 3). The values of $R_o$ are available in the literature [6, 11] on the respective depth intervals of the Khuff Formation. The comparison of $T_{max}$ and $R_o$ values allowed us to determine the correspondence between $R_o$ and $T_{max}$ for the section studied. On the basis of this relationship, we constructed the diagram $\delta^{13}C-R_o$ (Fig. 4). The $\delta^{13}C$ measurements of methane from the Kangan-Dalan Formation (zone D,E) correspond to $R_o$ values from 0.9 to 1.2%.

**Fig. 3.** Correlation between the parameters $T_{max}$ and $R_o$. Crosses show $T_{max}$ values obtained in this study. Shaded areas are $R_o$ intervals for similar rocks from gas fields of southern Iran and Abu Dhabi after [11].
Fig. 4. Results of analysis of δ\(^{13}\)C of methane from the gases studied versus \(R_o\) (\(T_{\text{max}}\)) of organic matter in the enclosing rocks. I and II are the empirical relationships of the isotopic composition of methane (δ\(^{13}\)C) and vitrinite reflectance (\(R_o\)) of gas-generating rocks for sapropel (14.81og\(R_o\), -41‰ ) and humic (8.61og\(R_o\), -28‰ ) organic matter, respectively [15, 16]. The dashed lines are theoretical curves [19, 25] approximating the empirical dependencies.

(1) Data for gases from Kangan and Dalan formations (zone D,E) and (2) data for gases from zone G.

These values correspond to the observed current degree of organic matter transformation in the Kangan-Dalan Formation. Thus, the source of gas in the gas fields of the Kangan-Dalan (zone D,E) could be represented by rocks of the same formation, for example, anhydrites from the middle part of the formation (zone F), which contain significant amounts of organic matter. However, older rocks could also be gas sources, for instance, the rocks of the Ordovician-Silurian complex. The degree of organic matter transformation in the latter now corresponds to \(R_o > 2\). However, Fig. 5, which illustrates the burial history of the sedimentary block in the area of Iran studied, demonstrates that the Ordovician-Silurian rocks occurred at the stage corresponding to the isotopic characteristics of gas in the Kangan-Dalan at about Late Jurassic-Early Cretaceous time. As was mentioned above, the Gahkom Formation of Ordovician-Silurian age contained graptolite shales with organic matter abundances of about 1.5%. These rocks could generate gas with the same geochemical characteristics as those now observed in gases from the Kangan field and zone D,E of the Dalan field. However, in this case, a new problem arises: how the gases passed the barrier of evaporite deposits, which occurs in the middle part of the Dalan Formation. Nowadays, the reservoirs above (zones C and D) and beneath the evaporite sequence (zone G) are evidently separated. Gases from zone G show significantly different chemical and isotopic compositions as compared to the gases of the Kangan-Dalan reservoir (zone D,E).

The depletion of methane from formation G could be caused by several factors. First, gases from zone G were probably generated later, when the Ordovician-Silurian rocks entered a zone of strong catagenesis. Now, the degree of organic matter transformation in the Gahkom Formation is estimated as \(R_o > 2\%\). Second, the depletion of hydrocarbon gases in the light isotope could result from the thermal reduction of sulfates.

Sulfate reduction phenomena are widespread in areas where anhydrites occur in the zone of severe catagenesis. This usually takes place upon sulfate burial at depths of 4-5 km [31, 32]. Sulfate is reduced due to reactions with organic carbon, including reactions with petroleum and gas hydrocarbons. Owing to the kinetic isotope effect, isotopically light molecules react more readily. This results, on the one hand, in the formation of isotopically light CO2 and calcite and, on the other hand, in the depletion of residual hydrocarbons in the light isotope. This effect is most clearly manifested in the isotopic composition of methane. It is conceivable that the anomalous (for methane) δ\(^{13}\)C values, such as -26.22 and -31.24‰ measured in the gases of zone G of the Dalan Formation are consequences of this process.

Warden et al [12, 33] pointed out the possible role of the process of the thermal chemical reduction of sulfates in the sedimentary section of southern Iran. It should be noted that the thermal chemical reduction of sulfate requires rather high temperatures, \(T > 140\)°C. Thus, this process could not be recorded in the compositions of gases from the Kangan-Dalan deposits (zone D). In contrast, in zone G of the Dalan Formation and in gases from underlying beds, the process of carbon isotope fractionation accompanying sulfate reduction could play an important role. In addition to the isotopic composition of methane, the isotopic characteristics
of CO₂ support this view. The process of sulfate reduction by organic compounds is accompanied by carbon oxidation and the formation of isotopically light biogenic CO₂. Carbon dioxide from zone G does show lower δ¹³C values (-21.87‰) than CO₂ from the upper part of the section (from -10 to -15‰).

**Fig. 5.** Burial history of sedimentary formations in the region of the Nar field (well 2). The diagram was constructed by computer modeling using the JENNEX program of the BEICIP-FRANLAB Petroleum Software Division.

The examination of the isotopic compositions of methane homologues: ethane and propane (Fig. 6) brought us to the same conclusions. In the upper part of the complex, in the Kangan rocks and zone D of the Dalan Formation, they show characteristics typical of catagenetic methane: methane is depleted in the light isotope relative to ethane, and ethane, in turn, relative to propane. In gases from the Kangan and zone D of Dalan, the values δ¹³C are higher by 9.5-10.5‰ than δ¹³C₁, and δ¹³C₃ are higher by 1.5‰ than δ¹³C₂. With an increasing degree of organic matter transformation, the difference between the isotopic compositions of methane, ethane, and propane decreases; i.e., the values δ¹³C of these hydrocarbons converge concurrently with changes in their absolute values [24, 25, 27]. The observed values δ¹³C₁, δ¹³C₂, and δ¹³C₃ in gases from the upper portion of the Kangan-Dalan section (zone D) correspond to Ro=1.0-1.2%, i.e., the degree of organic matter transformation in the enclosing rocks. In gases from zone G, δ¹³C of methane homologues records a higher degree of organic matter transformation and, moreover, falls off the normal dependency δ¹³C - Ro. As was mentioned above, inverse relationships were observed in the same cases: propane was isotopically lighter than ethane. This situation could result from the partial oxidation of hydrocarbons at the thermal chemical reduction of sulfates. The isotopic fractionation accompanying hydrocarbon oxidation is manifested more clearly in low molecular weight molecules. The residual methane can be significantly depleted in the light isotope. Ethane is more strongly depleted than propane. As a consequence, ethane, which was initially lighter than propane, can become isotopically heavier than propane. Such an effect was probably imprinted in gases from zone G.

The gas fields of both zone D and zone G bear condensate. The abundance of condensate is approximately 50 g per cubic meter of gas. Similar to the gases, the condensates show uniform carbon isotopic compositions in the Kangan Formation and the upper part of the Dalan Formation.
The carbon isotopic composition of the condensates varies from -27.37 to -28.72‰. These δ\textsuperscript{13}C values are rather low for condensate. Condensate generation may be related to two processes. Most often, it forms by the thermal destruction of petroleum [34]. Condensate of this origin usually shows a significant depletion in the light isotope relative to the average isotopic composition of the initial petroleum. The mechanism of isotopic fractionation resulting in the relative depletion of condensate in the light isotope was discussed in our previous publications [13]. When an oil pool descends into a high-temperature zone, the decomposition of medium-molecular-weight hydrocarbons (C\textsubscript{5}-C\textsubscript{12}), which chemically correspond to the condensates, results in the formation of hydrocarbon gases, in the polymerization of radicals, and in the generation of heavy petroleum and tar-asphaltene fractions. Owing to the kinetic isotopic effect, the products of this process, gases and tar-asphaltene substances, are enriched in the light isotope, while the residual fraction dominated by medium-molecular-weight substances, which compose the condensate, is enriched in the heavy carbon isotope. The isotopic composition of organic matter in the section studied, except for the graptolite shale, varies...
from -27.45 to -25.59‰, and that of the Silurian graptolite shales, from -31.19 to -29.36‰.

Bitumen associating with organic matter are characterized by average $\delta^{13}C$ values from -26.0 to -26.5‰ in the Kangan-Dalan deposits and -28.30‰ in the graptolite shale [36]. Approximately the same isotopic composition would be characteristic of the petroleum produced from the same organic matter. The condensates are isotopically similar to bitumen from the graptolite shale and show no depletion in the light carbon isotope compared to the possible initial petroleum. In other words, they are probably not products of the thermal transformation of petroleum.

Another mechanism of condensate formation is connected with gas-forming processes. In this case, condensate hydrocarbons are directly generated from kerogen. The gas is a carrier, which dissolves and transports hydrocarbons of the condensate fraction from the source rock. Condensates of this origin are typical, in particular, of hydrocarbon accumulations forming at the expense of the catagenesis of humic organic matter [19,37]. Humic organic matter is a typical gas-forming source. However, the gas-forming process could pre dominate in other cases also.

For example, if there is organic matter of a mixed origin. The sapropel component is a source of liquid hydrocarbon formation, which emigrates from the source rock and forms a gas condensate accumulation in the presence of methane, which is generated mainly from the humus component. It is important that the hydrocarbons composing such con-densates are formed directly by the destruction of organic matter rather than from previously formed hydrocarbons. Because of this, the mechanism of the depletion of condensates in the light carbon isotope is not realized in such a case. These condensates are inherently enriched in the light isotope [19].

The condensates accompanying Early Triassic-Late Permian (zone D) gases probably belong to the latter type. It is remarkable that the isotopic composition of condensate from zone G ($\delta^{13}C = -28.51‰$) is almost indistinguishable from that of condensates from the upper zone. This suggests genetic relationships between condensates from parts of the section underlying (zone G of Dalan) and overlying (Kangan and zone D of Dalan) the salt deposits. In contrast to gases, secondary processes including thermal chemical sulfate reduction could not change significantly the carbon isotopic composition of the condensate.

The condensates from zones D and G show somewhat different molecular compositions (Fig. 7). This distinction can be interpreted as smoothing by the secondary thermal destruction of molecular distribution in the condensate from zone G, which experienced a more severe epigenetic thermal history.

![Fig. 7. Distribution of n-alkanes in condensate from the (7) Kangan Formation, well 5 and (2) lower part of the Dalan Formation, well 22.](image)

Table 2 shows the pyrolysis characteristics of organic matter. It can be seen that the organic matter of the section shows relatively low hydrogen (HI) and oxygen (OI) indexes. This suggests a developed stage of the catagenesis of organic matter. On the van Krevelen diagram, the points of organic matter from zone G plot near the area of humic organic matter. This could also be related to a secondary alteration resulting, for instance, from organic matter oxidation at sulfate reduction. Indeed, the IR spectra (Fig. 8) of organic matter recovered from the anhydrite (zone F of the Dalan Formation) and the rocks of Ordovician-Silurian age show more pronounced absorption bands (1730 and 1160 cm$^{-1}$) corresponding to oxygen-bearing functional groups than the organic matter of the upper Dalan does.
### Table 2. Pyrolysis parameters of organic matter from the gas fields of southern Iran

<table>
<thead>
<tr>
<th>Field</th>
<th>Well no.</th>
<th>Formation</th>
<th>Zone</th>
<th>Depth</th>
<th>T&lt;sub&gt;max&lt;/sub&gt;</th>
<th>S&lt;sub&gt;1&lt;/sub&gt;</th>
<th>S&lt;sub&gt;2&lt;/sub&gt;</th>
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<th>OI</th>
<th>C&lt;sub&gt;org&lt;/sub&gt;</th>
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<td>0.55</td>
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**Fig. 8.** IR spectra of bitumen from the gas fields of southern Iran: (A) limestones of the Dalan Formation overlying salt member; (B) anhydrites of the Dalan Formation; and (C) graptolite shales of Ordovician-Silurian age. Numerals correspond to absorption bands, cm<sup>-1</sup>.

## CONCLUSIONS

Various hypotheses were proposed on the sources of large gas accumulations in the Permian-Triassic and Early Paleozoic deposits of the Persian Gulf zone, and the problem remains controversial. Some authors pointed out the probable gas-producing role of the Ordovician-Silurian shales of the Gahkom Formation [9-11, 38]. Beydoun [1] argued that the Permian gas could be genetically related both to the Permian rocks and the rocks of the Early Paleozoic after their passing through the "petroleum window" stage. Organic matter from the Dalan anhydrite was also considered as a possible source of gases within...
The results presented in this paper allow us to constrain for the first time the source of Paleozoic gases in southern Iran on the basis of the geochemical characteristics of hydrocarbons. First of all, we can conclude that gas pools in the carbonate rocks of the Early Triassic (Kangan Formation) and in the Late Permian Formation overlying salt beds (Dalan Formation, zone D,E) represent a single gas reservoir, the gas there having fairly uniform geochemical characteristics throughout the entire section.

The carbon isotopic composition of methane and its homologues is compatible with the suggestion that their source may have been rocks of almost the same age, in particular, Dalan dolomites and anhydrites.

Gases from the Dalan Formation occurring below the anhydrite sequence are characterized by specific geochemical and isotopic parameters. At first glance, this suggests fundamentally different gas sources for deposits overlying and underlying salt sequences. Nevertheless, it is possible that these gases were derived from a single source and that the gases from the lower zone (zone G) were affected by secondary alteration and were generated at a later stage of the catagenetic evolution of parental sediments. There are several lines of evidence that support such a supposition.

The significant depletion of methane in the light carbon isotope and the inverse relationships of the isotopic compositions of ethane and propane in gases from the underlying deposits most likely result from their partial oxidation (accompanied by the isotopic effect) in the process of thermal chemical sulfate reduction:

\[
\text{SO}_4^{2-} + \text{CH}_4 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + S^{2-}
\]

Carbon dioxide forming in this reaction at the expense of isotopically light organic carbon must be enriched in the light isotope. This was observed, \(\delta^{13}C_{\text{CO}_2} = -21.87\%\text{oo}\), in a gas sample from zone G in contrast to \(\delta^{13}C_{\text{CO}_2} = -10...-15\%\text{oo}\) in gases from zone D.

In the sulfate reduction zone, organic matter (kerogen) is partially oxidized and enriched in oxygen-bearing functional groups:

\[
\text{SO}_4^{2-} + \text{C}_x\text{H}_y\text{O}_z \rightarrow S^{2-} + \text{CO}_2 + \text{H}_2\text{O} + C_{x-1}\text{H}_{y-2}\text{O}_{z+1}
\]

This process is recorded in the IR spectra of organic matter from the Dalan anhydrite and the rocks of the Lower Paleozoic section, whose absorption bands corresponding to oxygen-bearing groups are more intense than in the carbonates overlying the salt sequence.

On the van Krevelen diagram, the points of organic matter from the Ordovician-Silurian deposits fall on the evolution line of humic organic matter, although the humic organic matter proper, i.e., material of continental origin, could not be characteristic of Early Paleozoic time. The relatively high OI probably resulted from secondary oxidation of this organic matter.

It is characteristic that the carbon isotopic compositions of condensates, whose isotope signature could not be much affected by partial oxidation, are essentially identical in the upper Kangan-Dalan reservoir (zone D,E) and in the deposits underlying salt beds (zone G). Moreover, the isotopic compositions of condensates are most compatible with their formation from the organic matter of the Early Paleozoic graptolite shales. The occurrence of condensates of essentially identical compositions in gases of both the upper and lower parts of the section is an argument for the common genesis of the gases that comprise them.

Condensates from the lower part of the Dalan Formation bear evidence of additional thermal influence, which is quite understandable. The isotopic composition of gases from the lower part of the section also evidently changed in the process of secondary oxidation and as a result of its formation at a later stage of katagensis of the initial organic matter. Both factors affected isotopic parameters to some degree in a single direction.

Thus, the following model of formation of gas accumulations in the Permian-Triassic deposits of southern Iran seems to be most plausible.

The generation of gas accompanied by condensate commenced when the Ordovician-Silurian rocks passed into a catagenesis stage corresponding to \(\text{Ro} = 1.0-1.2\%\), which probably took place at the end of the Jurassic and the beginning of the Cretaceous. Gas formation proceeded concurrently with the burial of the sedimentary prism. Younger deposits including Permian ones entered the phase of gas generation. The Permian-Triassic collector was filled with gas. The subsequent gas portions and condensate accumulated the lower part of the Paleozoic section. At that time both graptolite shales and anhydrites occurred at depths where the process of thermal chemical sulfate reduction exerted a considerable effect on the composition of gases and organic matter. As a consequence, the observed geochemical characteristics of gases of the lower zone were formed, which were significantly different from those of gases from the upper zone.
REFERENCES

27. James, A.T., Correlation of Natural Gas by Use of Carbon Isotopic Distribution between Hydrocarbon


