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THE RELATION BETWEEN ISOTOPIC COMPOSITION OF ARGON AND CARBON IN NATURAL GASES

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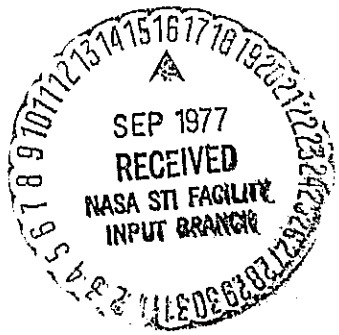

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16. Abstract

The methods and results of determination of the argon and carbon isotope compositions of hydrocarbon gases of Mezozoic complexes of Western Siberia are presented. A linear relationship exists between atmospheric argon and $\delta^{13}C$ of the various deposits. Based on the ^{36}Ar, ^{40}Ar, ^{12}C, and ^{13}C content of the various deposits and on the presumed mechanisms of entry of these isotopes into the deposits, it is concluded that formation of natural gas in some deposits included vertical migration from a lower complex.

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THE RELATION BETWEEN ISOTOPIC COMPOSITION OF ARGON AND CARBON IN NATURAL GASES

Ye.Ya. Gavrilov, Yu. A. Zhurov, and G.I. Teplinskiy

In study of the isotope composition of carbon and argon /448* in the hydrocarbon gases of the Mesozoic complexes of Western Siberia, a relation of the isotope composition of the carbon of methane to the content of atmospheric argon in the gas was first found. This relation of the isotope composition of carbon and argon in natural gases should reflect the general regularities of formation of the isotope composition of these elements. This is of indisputable theoretical and practical interest.

Gases of the Pokurskaya series and its analogs (Aptian-Albian-Senomanian) and Valanginian and Jurassic locations were studied. The gases were sampled in metal containers under pressure, which excluded the intake of atmospheric argon from the atmosphere. The separation and quantitative measurement of argon were carried out in a Khlopin-Gering type installation, with structural changes for determination of the argon content of the gases. The isotope composition measurements were carried out in a type MI-1305 mass spectrometer, by the triple beam method, using a two channel inlet system with electromagnetic valves. Atmospheric argon was used as the standard. Measurement accuracy was at least $\pm$ 1.5%. The excess argon-40 was calculated by the relation (%):

$$^{40}Ar_{ex} = \frac{(^{36}Ar/^{40}Ar)_{air} - (^{36}Ar/^{40}Ar)_{sample}}{(^{36}Ar/^{40}Ar)_{air}}$$

The isotope composition of the carbon was determined by methods described earlier [1,2]. The results are presented in the values of $\delta^{13}C$, relative to the internation PDB standard. The accuracy of

*Numbers in the margin indicate pagination in the foreign text.

determination of $\delta^{13}C$ was $\pm$ 0.05%. The methane was extracted by fractionation of the hydrocarbons.

The measurement results are presented in Table 1. A curve of the isotope composition of the carbon of methane vs. atmospheric argon content was plotted from these data. To explain the linear relation, some questions of the geochemistry of the carbon and argon isotopes, as well as the specific conditions of formation of the gas deposits of Western Siberia, must be examined.

Table 1

ISOTOPE COMPOSITION OF METHANE CARBON AND ARGON OF NATURAL GASES

a Месторождение	b № скв.	c Интервал перфорации, м	d Возраст коллектора	e $Ar_{общ}$, ч.н.м.	f $Ar^{40}_{изб}$, %	g $Ar_{рад}$, ч.н.м.	h $Ar_{возд}$, ч.н.м.	$\delta C^{13}_{CH_4}$, %
1 Вингаяхское	3	794—796	Cr_3sm	116,7	6,2	7,2	109,5	—6,03
2 Комсомольское	7	971—977	То же	89,3	10,3	9,2	80,1	—5,47
3 Ыдинское	6	1148—1176	» »	68,1	8,4	5,7	62,4	—5,29
4 Уренгойское	13	1280—1230	» »	63,2	9,1	5,8	57,4	—5,02
5 Медвежье	12	1132—1188	» »	58,8	14,3	8,4	50,4	—4,93
Медвежье	11	1139—1165	» »	56,4	13,5	7,6	48,8	—4,91
6 Мессояхское	P-9	833—839	» »	26,5	31,8	8,4	18,1	—4,11
7 Новопортовское	79	1796—1802	Cr_1vlg	12,1	53,4	6,5	5,5	—
Новопортовское	79	1828—1835	То же	7,2	53,9	3,9	3,3	—3,96
8 Уренгойское	17	3000—3020	J	8,2	59,7	4,9	3,3	—3,84

Key: a. Deposit
b. Well #
c. Drilling interval m
d. Reservoir age
e. Ar_{total}, ppm
f. $^{40}Ar_{ex}$, %
g. Ar_{rad}, ppm
h. Ar_{air}, ppm
i. Same

1. Vengayakhskoye
2. Komsomol'skoye
3. Nydinskoye
4. Urengoyskoye
5. Medvezh'ye
6. Messoyakhskoye
7. Novoportovskoye
8. Urengoyskoye

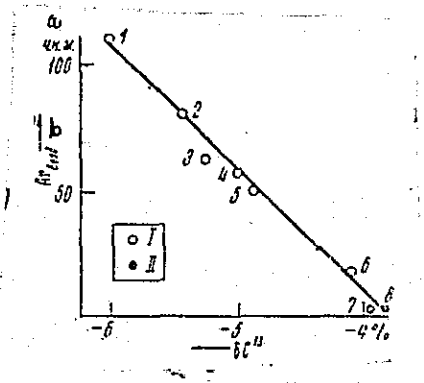

Fig. 1. 1. Vengayakhskoye, 2. Komsomol'skoye, 3. Nydinskoye, 4. Urengoyskoye, 5. Medvezh'ye, 6. Messoyakhskoye, 7. Novoportovskoye, 8. Urengoyskoye deposits; I. Senomanian deposits; II. Jurassic and Valanginian deposits.

Key: a. ppm
b. Ar_{air}

It is seen from Table 1 and Fig. 1 that the atmospheric argon content of the Jurassic and Valanginian deposit gases, which are marine fascies, is significantly less (3.5-5.5 ppm[1]), than that in the Senomanian continental formations (18.1-109.5 ppm). According to the model of V.P. Savchenko [3], atmospheric argon enters the gas formations from connate waters, which previously were in equilibrium with the air. Under these conditions, the maximum possible vapor pressure of atmospheric argon in the formations, in reaching phase equilibrium, is determined by the temperature and mineralization of the water in the sedimentation basin, on the one hand, and by change in these parameters during burial of the deposits, on the other hand. However, the difference in concentration of atmospheric argon in the gases of the upper and lower complexes cannot be explained by a change in solubility of the atmospheric argon with different mineralization of the initial sedimentation basins or by change in temperature of the connate waters alone, since the difference in argon concentration in this case is not over 1.5-2 fold. /449

The change in argon vapor pressure in the gas formations is not changed by the phase equilibrium mechanism alone. Argon from the bedding system can be removed together with the hydrocarbons,

[1]ppm - parts per million.

by migration of the latter in the gas phase. In this case, the connate waters, which are the supplier of argon to the gas formation, are depleted of argon [4], which determines a reduction in the maximum possible vapor pressure in the newly formed gas formation. With the migration of hydrocarbons from the bedding system, both atmospheric and radiogenic argon are lost. The fact that radiogenic argon is continually generated and enters the bedding system and the atmospheric, in the absence of active infiltration water exchange, is not replenished, leads to the situation that the percentage of radiogenic argon in total argon increases with the passage of time.

The low Ar_{air} and Ar_{rad} concentrations, as well as the increase in Ar_{ex} concentration in the gases of the Jurassic and Valanginian deposits can be explained by the export of argon by the hydrocarbon gases to the atmosphere, before deposition of a clay covering during the Valanginian. There was less migration of gases to the atmoshpere from the Senomanian deposits, in connection with the fact that the regional Turonian-Paleogene clay cover developed before submergence of the parent gas formation into the catagenesis zone, i.e., before the beginning of active gas formation in the Pokurskaya series. The assumption made, of large scale loss of gas from the lower complex, is confirmed by the distribution of radiogenic argon, the content of which in the Senomanian deposit gases averages 1.5 times that of the Jurassic and Valanginian deposit gases. In this case, the possibility of post-Valanginian vertical migration of the hydrocarbons through lithofascial windows of the Valanginian covering is not excluded since the latter was not maintained lithologically. This process leads to the entry of gases into the upper complex, which are depleted of Ar_{air}. This should cause a reduction in its concentration in the Senomanian formation gases. The mixing of

syngeneic gases of the Pokurskaya series with gases of the lower complex in various proportions was the cause of wide variations in the atmospheric argon content of the upper complex gases. In /450 this case, migration of the gas from the lower complex to the upper was accompanied by its enrichment in methane, compared with the heavier hydrocarbons [5].

The role of vertical migration in the formation of the Senomanian formations was noted earlier [6,7]; together with this, a number of authors [8,9] deny the possibility of the development of vertical migration in this region. Recently, works [10,11] have been published, in which an attempt is made, on the basis of differences in isotope composition of the carbon of the gases of the two complexes, to confirm the latter point of view, without considering the variations in isotope composition of carbon within the complexes, in this case.

A combined examination of the isotope composition of carbon and argon and determination of the relations between the isotopes of these elements has permitted a new interpretation of the experimental data.

On consideration that the methane formed at various stages of conversion of organic matter was more enriched in the light isotope ^{12}C than the methane of the latter stages of gas generation [12], it can be assumed that the losses of the hydrocarbons of early stages of gas generation of the gas parent deposits in vertical migration leads, in the general case, to an increase in the contrast of the isotope composition of carbon of the methane of the gas formations located at different depths. Consequently, the same process, the process of the loss of gas by the parent gas deposits, leads to a unidirectional change in the isotope composition of both the methane carbon and argon.

If it is assumed that the gas of the Senomanian formation of the Vengayakhskoye deposit is syngeneic, to decide from the maximum atmospheric argon concentration (109.5 ppm) and from the minimum ^{13}C isotope content of the methane ($\delta^{13}C = -6.03\%$), the variations in isotope composition of carbon can be explained by mixing of the syngeneic gases and those migrating from the lower complex, in which the fraction of the migrating gases differs in different formations. It is at a maximum in the gas of the Messoyakhskoye deposit, exceeding 75%. The correctness of this assumption is confirmed by the linear relation between Ar_{air} and $\delta^{13}C$.

Thus, the conditions of formation of gas deposits affects the distribution of the argon and carbon isotopes in the formations to a considerable degree, and joint study of them can be a supplementary demonstration of the conditions of the migration and accumulation of natural gases. Such a combined study of the isotope composition of the elements has already yielded positive results. Thus, a study of the carbon and sulfur isotopes [13,14] has enabled the basic features of native sulfur deposits to be determined and a number of questions on the genesis of sulfur deposits to be answered.

The combined study of the isotope composition of carbon and argon in natural gases we have performed provides a qualitatively new possibility of interpretation of the conditions of formation of gas deposits.

It should be noted in conclusion that atmospheric argon is found, not only in the free and dissolved gases of sedimentary strata, but in the gases of all minerals studied, of both sedimentary and magmatic rock. This permits the use of data on the

atmospheric argon content in both gas geology, and in the answering of questions relating to determination of the conditions of lithogenesis and metamorphism of sedimentary rock.

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