

Some aspects of natural gases distribution on the territory of Georgia

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Резюме. Във връзка с изпълнение на проект ERA-NET „Natural Analogue investigation for CCS in the Southern Caucasus” група от Научно-изследователския център по геофизика и геотермия изучава разпространението на природните газове в подземните води на територия на Грузия. За полевите изследвания бе създаден мобилен отряд, който се движеше по предварително определен маршрут със специално оборудван за целта автомобил и проведе опробване от естествени и изкуствени източници. При полевите измервания бе използван уредът WTW340i (за рН, електропроводност, температура, свободен кислород), а също ОСВК INGEM-1 за определяне на радон и хелий. Освен това бяхме снабдени и със специално оборудване рGD3-IR за измерване на съдържанията на газове (CH₄, O₂, CO₂ и H₂S). В определени пунктове бяха взети проби и за химичен анализ (Na, Ca, K, Mg, HCO₃, SO₄ и Cl) и стабилни изотопи (¹⁸O, ²H), които бяха анализирани в лаборатория в Тбилиси.

Газовете в подземните води бяха изследвани в тяхното естествено състояние, а също и в сондажи. Повечето установени газови проявления са свързани минерални води, а друга част - към нефтени натрупвания, някои от които са довели до образуване на газови залежи. Както се и очакваше, разпределението им е свързано с геоложкия строеж на Грузия. Газсъдържащите зони с определени компоненти и геохимични особености имат еднакви направления. Могат да се разграничат следните зони:

1. Северна зона, съдържаща въглероден диоксид;
2. Централна зона - с метан и азот;
3. Южна зона - със съдържания на азот и въглероден диоксид.

Северната зона съвпада с две геотектонски единици - Главната Кавказска антиклинала и Южния склон Главния Кавказски хребет без крайните сегменти на изток и запад. В газовите комплекси на тези зони, които са свързани главно с находища на минерални води, явно доминира въглената киселина. По-голяма част от тези проявления са свързани с находището Нарзан, представляващо основния вид минерални води на тази територия. Въглеродният диоксид е привързан към главния тектонски възсед и неговите предичание с меридиални разломи, а също и с образувалите се по тях реки като Ингури, Цхенис Цкали, Риони, Диди Лиавхи, Терек, Арагви, Аргуни и др. Съдържанието на свободния въглероден диоксид в подземните води на северната зона е приблизително 1 g/l, понякога повече от 2 g/l. Такива високи концентрации на въглероден диоксид и тяхната връзка с определени типове повърхностни и подземни води доказва генетична връзка на въглеродния диоксид с магмени и метаморфни процеси. В северната зона освен въглероден диоксид се установяват газови асоциации от смесен тип. Установени са области с присъствие на азот в количества десетици процента. Причината за появата на азот е активната циркулация на атмосферни валежи в зоната на изветряне, където кислородът активно се изразходва за окислителни реакции.

Централната зона се характеризира с наличие на метан и азот и обхваща територията на

междупланинската част на Грузия и някои гранични региони - Южния блок на Голям Кавказ и склоновете на Аджария-Триалети. В спомената по-горе зона метанът несъмнено има органичен произход и се среща главно при комплексното му взаимодействие с подземните води, а също и във вид на газ, присъстващ в нефта. Като се има предвид отношението Ag/N_2 , основната част от азота има атмосферен произход и е свързан с циркулиращи в открити хидрогеоложки структури подземни води. Следователно структурните особености на тази област определят условията за присъствието на тези два компонента. Резултатите от газовите анализи показват съществени разлики между горно- и долнокредните седименти според изграждащия ги материал. Като правило в долнокредните скали се установяват оксиди на азота, докато в горнокредните преобладава метана. Това се дължи на ясни различия в акумулирането и условията за натрупване на газове в тях, изразяващи се в ограничения режим на движение в горните хоризонти и по-добрата проводимост на долните. В тях са установени различни стойности на минерализацията на подземните води (по-малко от 1 g/l в долнокредните седименти и значително по-високи в горнокредните) и различна възраст на системата „газ + вода” (He/Ag за долнокредните отложения е 5-10 пъти по-ниско, отколкото за подземните води в горната креда). Източната част постепенно затъва в югоизточна посока към газ-съдържащата централна зона. Съответно, в гореспоменатите територии присъствие на газове е установено в кредните скали на източната част (Сурами, Горижвари), в еоцена на средната част (Тбилиси), в миоцена (Норио), в горния миоцен и плиоцен на източната част (Дедоплис Цқаро, Мирзаани, Гурджаани, Патара Шираки и т.д.). Присъствието на метан в описаната територия най-често се проявява в източна посока при Норио-Марткопи, в района на реките Йори, Патара Шираки и др. Най-добре газовете са изучени в района на реката Йори. Горливите газове, които достигат до повърхността заедно с нефта, се характеризират с пълно отсъствие на хомоложката група на метана.

В Южната зона проявленията на газовете обхващат голяма част от нагънатата зона Аджария-Триалети и блока Артвин-Болниси. Има многобройни проявления въглероден диоксид. Газовият фактор на групата Боржоми, а също Вардзия, Накалакеви и др. често достига 7-10 g/l. Освен това налягането в хоризонтите е много високо (25 атмосфери в сондаж). Понякога на много места се установяват сухи изгичания на въглероден диоксид, като стойностите му достигат до 2 g/l. Това свидетелства за съществена силна ескалация на въглеродния диоксид. Не може да има съмнение за връзката между въглеродния диоксид и постмагматичните процеси. Освен това установените тук кватернерни лави също са доказателство за неотдавнашна вулканска активност. В района на Боржомските минерални води основната част от проявленията на въглеродния диоксид са привързани към по-стари скали - долнокредни. Газираните с въглена киселина минерални води се отнасят към хидрогенкарбонатно-натриевия тип и са с ниска минерализация, държаща се на смесване с повърхностни води. Разпределението на азота в южната зона е значително, но има по-малка роля, отколкото тази на газовете вследствие на въглената киселина. Основно азотът е разпространен в средноеоценските вулканични образувания и под долноеоценския и плиоценски флиш. Азотсъдържащите води представляват терми с различен химичен състав и минерализация.

Сероводородни води присъстват по цялата територия на Грузия, особено в централната зона. Изучавайки произхода на сероводорода, може да се направи извод, че в централните и в голяма част от южните зони той е свързан с метана и често с натрий-хлорни води. Определящ фактор се явява биохимическият процес на органично разлагане. Главен фактор за присъствието на сероводород в нискоминерализираните термални води се явява процесът на разрушаване на пирита, който е често срещан минерал в юрските скали на южните склонове на Голям Кавказ и във вулканските образувания на средния еоцен в района на Аджаро-Триалети.

Ключови думи: природни газове, извори, Грузия

Abstract. Natural gases possess a vast impact in the formation of groundwater physical and chemical properties. Most of them are connected with the mineral waters, the rest of their exposures are represented as “oil” gases or as a gas accumulation areas. Natural gases are very sensitive indicators of geological, in particular, of geotectonic conditions. Thus, as it should be expected, the distribution pattern of natural gases clearly reveals the particularities of the geological structure on the territory of Georgia. The geotectonic elements, which are allocated within these borders, in accordance with the folding, the geological development age and history, are characterized by the corresponding gas compositions and geochemical properties.

Keywords: natural gases, springs, Georgia

Introduction

Within the frame of ERA-NET project „Natural Analogue investigation for CCS in the Southern Caucasus” the Georgian group from Research Center of Hydrogeophysics and Geothermic carried out a gas mapping on the whole territory of Georgia. During the field studies the mobile group was moving on with equipped with special devices car along the pre-defined routs while sampling springs and boreholes. For the field measurements WTW340i (for pH, conductivity, temperature, free oxygen) as well as SISE and INGEM-1 for Radon and Helium measurements were used. Also, the apparatus PGD3-IR for gas measuring (CH_4 , O_2 , CO_2 and H_2S) was used. Some selected points were sampled for a typical chemical analysis (Na, Ca, K, Mg, HCO_3 , SO_4 and Cl) done at the laboratory (Tbilisi).

Discharges of natural gases are observed in the springs as well as in the boreholes. The most of them are linked with mineral waters and some of them are revealed as ones accompanying crude oil or gas deposits.

Data analysis

The geotectonic elements distinguished at the territory of Georgia in accordance to their folding, age and history of geological development are widely distributed in Caucasus (Gudjabidze, 2003). In similarity, the gas conductivity zones with certain components and their geochemical features could be observed (Fig. 1). Among them are as follows:

1. The Northern zone of Great Caucasus System;
2. The Central zone of Georgian plate system;
3. The Southern zone of Adhara-Trialeti and Artvin-Bolnisi system.

The Northern zone contains two geotectonic elements – the main Caucasian anticline block and the Great Caucasian folded ridge without the edge segments in the East and West.



Fig. 1. International group gathering Georgian, German and Bulgarian colleagues during a sampling works in Kazbegi region.

Фиг. 1. Международен екип от грузински, немски и български специалисти по време на взимане на проби в област Казбег

The gas associations of these zones are related especially to the “Narzan” type springs- to the main type of mineral waters in the investigated territory (Buachidze, 1970; Bagoshvili, 1990). Natural gases obviously discharge along the latitudinal tectonic rocks, in particular near the main displacement and their crossings with rivers canyon, such as, Enguri, Tskhenis Tskali, Rioni, Didi Liakhvi, Tergi, Aragvi, Arghuni, etc. The situation allows studying them along these river basins. In gas composition carbonic acid is highly dominant (Table 1).

Table 1. Typical gases composition of water on the territory of Georgia

Табл. 1. Примерен газов състав на водите на територията на Грузия

№	Location	Water physical parameters				Water chemical parameters				
		T °C	pH	Discharge l/s	Gas-factor	CO ₂ %	CH ₄ %	N ₂ %	Rn Bq/l	He 10 ⁻⁵ ml/l
North Georgia										
1	Achkhoti	10	5.9	0.3	0.4	89.1	9.8	1.1	37.7	20
2	Stepancmindsa	11	5.4	0.5	0.5	87.5	9	3.5	1056.6	545
3	Nenskra	10	5.7	0.3	0.6	99.6	0.3	0.1	130	40
South Georgia										
4	Vardzia	35	6.4	0.5	7	99.8		0.1	450	120
5	Vashlovani	40	7	0.3	0.8	69.3	21.8	8.9	145	36.5
6	Kvibisi	38	6.5	0.1	0.7	40	30	30	134	40
West Georgia										
7	Chaladidi	70	8	0.4	0.2	9	11	80	160	35.7
8	Kvaloni	94	7.5	0.3	0.3	-	65.4	34.6	134	17
9	Ompareti	84	7.3	0.5	0.2	-	1	99	144	16
East Georgia										
10	Kvareli	24	7.1	0.4	0.2	-	57	43	200	22
11	Mirzaani	22	7.2	0.2	0.1	10	68	22	65	15
12	Norio	25	7.5	0.3	0.3		72	28	102	35

In the basin of the river Tergi, Kazbegi region, gases are related with mineral waters of hydrocarbonate-chloride, sodium-calcium type, with total dissolved solids (TDS) between 0.7 to 5.5 g/l. Concentration of carbon dioxide is approximately 1 g/l, sometimes – more than 2 g/l. In this group exposure of gases is especially frequent and they are placed in a linear way that is caused by their connection with tectonic structures (Fig. 2)(Melikadze et al., 2013).

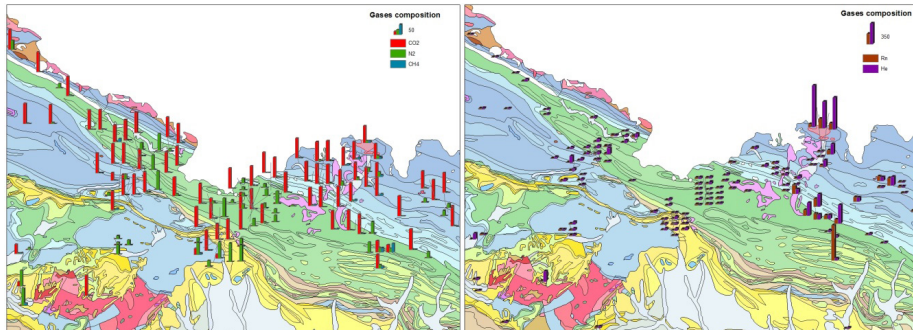


Fig. 2. Natural CO₂, CH₄, N₂ (left) and Rn, He (right) gases distribution in the Northern zone

Фиг. 2. Разпространение на естествени газове CO₂, CH₄, N₂ (вляво) и Rn, He (вдясно) в Северната Зона

Such a high content of carbon dioxide is related to the certain type of groundwater and indicates the genetic connection of magmatic-metamorphic processes with carbon dioxide presence. Therefore, it could be concluded that carbon dioxide is of a volcanic genesis.

To the South, the group of gas exposure in the upper basin of the river Aragvi

is connected with hydrocarbonate and sodium-calcium waters with TDS up to 5 g/l. With higher TDS (usually 7-20 g/l, seldom – up to 38 g/l) and hydrocarbonate-chloride (Chargali, Kharanaulta) and chloride-hydrocarbonate (Pasanauri, Likoki, Atabe) sodium waters, the content of carbon dioxide, with the exception of some rare cases, exceeds 97%. High concentrations of gases Radon and Helium are observed in the regional fault system zone, what can be explained by high gas permeability of this type of deep fault system (Fig. 2, 3).

In the Northern zone, besides carbon dioxide gas exposure, there are observed some mixed type of gas associations. In natural gases sometimes we find nitrogen from few up to several tens of percentages. There are also pure nitrogen exposures, namely Pskhu and Torghvasabano. Compared to the carbon dioxide gas exposure they are less detected. Nitrogen content in local mineral waters is not more than 0.05 g/l. Lack of organic material does not allow considering abundance in biogenic nitrogen, even the value of argon-nitrogen interaction refers to its atmospheric genesis. It is also referred by “gas+water” system depended on He/Ar correlation. This value for carbon dioxide associations is one and a half to five times higher.



Fig. 3 “Sortuani” and “Utsera” district, Racha region
Фиг. 3. Райони „Сортуани” и „Уцера”, регион Рача

The reason for a nitrogen gas exposure is the intense circulation of the precipitation in the fractured-erosion zone when oxygen is intensively spent on oxidation reactions.

By the gas content, the Central zone is mainly characterized by methane and nitrogen distribution and it covers the territory of intermountain area of Georgia and some adjacent regions – the southern block of Great Caucasus Mountains and Adjara-Trialeti slope.

Despite the numerous borehole investigations of on this territory, the natural gases content has not been studied sufficiently. In addition, taking into account the variety and structural complexity of the soil it becomes difficult to clarify the geochemical zonation of natural gases. Nevertheless, the common features of the zones can be considered as follows:

On the abovementioned zone the presented methane doubtlessly is of an organic origin and is found mainly in complex circulation with waters as well as in the form of a gas accompanying the crude oil. According to the Ar/N₂ correlation the nitrogen is of an atmospheric origin and is related with groundwaters which circulate in the hydro-geologically open structures. Consequently, the structural properties of the area define the development conditions of these two main components.

The nitrogen gas is main component of gas discharge from the Jurassic age sediments residues in the periphery of the Kolkheti lowland. The upper and lower Cretaceous sediments are quite different from each other in respect of the composition of materials releasing gases. Usually, nitrogen content in natural gases is related to the lower Cretaceous age aquifers, when upper Cretaceous aquifer

gases have methane composition. This is explained by the clear difference in the gas accumulation and storage conditions in the upper and lower Cretaceous sediments expressed by the existence of limited conductivity in the upper Cretaceous aquifer and good water conductivity in the lower Cretaceous one. It results in different degrees of TDS of the groundwaters (less than 1 g/l for lower Cretaceous waters and significantly higher for upper Cretaceous waters) and different age of the “gas+water” system.

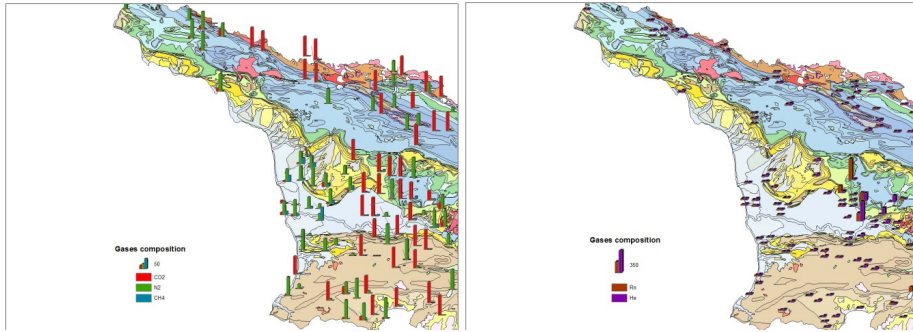


Fig. 4. Natural CO_2 , CH_4 , N_2 (left) and Rn, He (right) gases distribution in the West Georgia.

Фиг. 4. Разпространение на естествените газове CO_2 , CH_4 , N_2 (вляво) и Rn, He (вдясно) в Западна Грузия

In the West Georgia, the high concentration of gas Radon and Helium are observed in Tskaltubo region where deep fault systems are presented (Fig. 4, 5) (Amiranashvili et al., 2008; Melikadze et al., 2009; Vaupotic et al., 2012).



Fig. 5. “Tsaishi” and “Nokalakevi” thermal boreholes

Фиг. 5. Каптажжи за термална вода „Цайиши“ и „Нокалакеви“

The Eastern part of Central zone is gradually sinking to the south-east direction. Consequently, on the abovementioned territories the following gas exposures are detected: - in the Cretaceous sediments of eastern parts (Surami, Gorijvari), in the Eocene of the middle part (Tbilisi), Miocene (Norio), in the upper Miocene and Pliocene of the eastern part (Dedoplis Tskaro, Mirzaani, Gurjaani, Patara Shiraki, etc.). Methane exposure is more frequently revealed to the eastern direction and is connected mainly with the existence of crude oil in the sediments at Norio-Martkopi, Patara Shiraki, along Iori River and others. In the gas content, together with methane, hydrocarbons and biogenic nitrogen are found, which characterizes the young fresh aquifers. Gas discharge has been better studied in the area of Alazani and Iori rivers. Flammable gases released on the surface together with

the crude oil are characterized with full absence of homological group of methane (Buachidze, Zedginidze, 1985; Gaprindashvili, 2002; Melikadze, 2014; Buachidze, 2005; Sima, 2013).

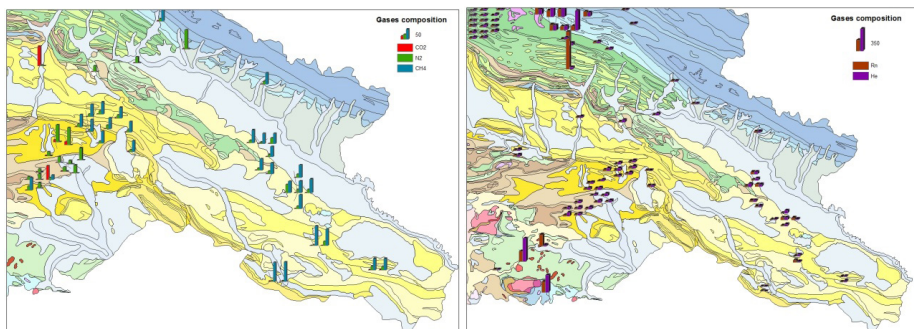


Fig. 6 Natural CO_2 , CH_4 , N_2 (left) and Rn , He (right) gases distribution in the East Georgia

Фиг. 6. Разпространение на естествените газове CO_2 , CH_4 , N_2 (вляво) и Rn , He (вдясно) в Източна Грузия

In the East Georgia (Fig. 6) low concentrations of Radon and Helium gases are observed in the plate system.

At the Southern zone the gas exposure covers the most part of Adjara-Trialeti folded system and Artvin-Bolnisi block (Fig. 7). The central part of the mentioned zone is characterized by hydrologic solubility that is a negative factor for gas accumulation. There are numerous carbon dioxide gas discharge areas in the Southern zone. The gas factor of Borjomi group as well as Vardzia, Nakalakevi and others often reach 7-10 (Fig. 5, 8). Besides, the horizon pressure is quite high (25 atmospheres in a borehole). Dry outlets of carbon dioxide gas are also observed rarely. The amount of exposed carbon dioxide reaches up to 2 g/l.

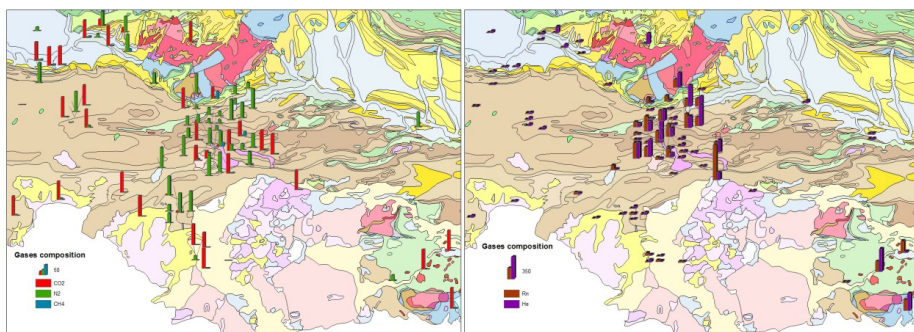


Fig. 7 Natural CO_2 , CH_4 , N_2 (left) and Rn , He (right) gases distribution in the South zone

Фиг. 7. Разпространение на естествените газове CO_2 , CH_4 , N_2 (вляво) и Rn , He (вдясно) в Южната Зона

All the above mentioned facts refer to the existence of strong carbon dioxide emission. Genetic links of carbon dioxide and the young post-magmatic processes cannot be doubtful; besides, the discovered Quaternary lava here refers to the recent volcanic activity.

Based on data about Borjomi mineral waters, we can assume, that the main portion of carbon dioxide is related to the upper Cretaceous sediments. Mineral



Fig. 8. Mineral water boreholes “Borjomi” (left) and “Aspindza” (right)
 Фиг. 8. Каптажѝ за минерална вода „Боржомѝ” (вляво) и „Аспѝндза” (вдясно)

waters gassed by CO₂ belong to hydrocarbonate sodium type possessing low TDS caused by mixing with fresh waters (Melikadze et al., 2009a; Melikadze et al., 2011).

Nitrogen distribution in the Southern zone is significant, but much less than the exposures of carbon dioxide gases. Nitrogen is mainly found in the middle Eocene volcanic formations and in the lower Eocene and Paleocene flysch. The nitrogen containing waters are thermal ones with different chemical composition and low TDS (Aspindza, Tsikhis Jvari, Dviri, Atskuri, Abastumani, Abano, Makhindjauri, etc.).

Sometimes detected carbon dioxide -nitrogen gas exposures are of a mixed type: nitrogen of atmospheric genesis with carbonic acid gases of abyssal genesis. The fact is predetermined by the mixing character of the groundwaters to which these gases are associated.

Within the Georgian territory on the Artvini-Bolnisi plate only three gas exposures have been observed in the boreholes in Nakalakevi, Vardzia, Bolnisi. Despite the lack of factual material, it is quite reasonable to assume an existence of carbon dioxide in the rest parts of the territory, under the lava body.

Hydrogen sulfide gas composition type waters are met over the whole territory of Georgia, especially in the Central zone. It is connected with the decomposition process of pyrite, which is a widely distributed mineral in the Jurassic rocks of the Greater Caucasus southern slopes and in the Adjara-Trialeti middle Eocene volcanic formations.

Discussion

As showed the characteristics of gas distribution is pre-conditioned by the geological structure of the territory of Georgia and its modern geodynamical activity. In particular, carbon dioxide rich zones are located in the South and North regions, and its emission is related to the recent volcanic activity (Fig. 9). These areas are bounded by two conventional sub-meridian faults: the first- the connecting line of an old continental reefs and the second one - the anti-Caucasian direction branch line of regional Anatolian fault. On the territory of among these two lines is observed carbon-dioxide gas as a dominant.

On the rest territory of Great and Lesser Caucasus mountain ranges nitrogen gas stands as dominant, which is explained by the presence of active groundwater exchange systems. However, it should be noted, that there are some conventional transition zones, where as a rule the both gas are observed: the nitrogen from the active circulation zone - surface water and carbon-dioxide from the deeper circulating groundwaters zone.

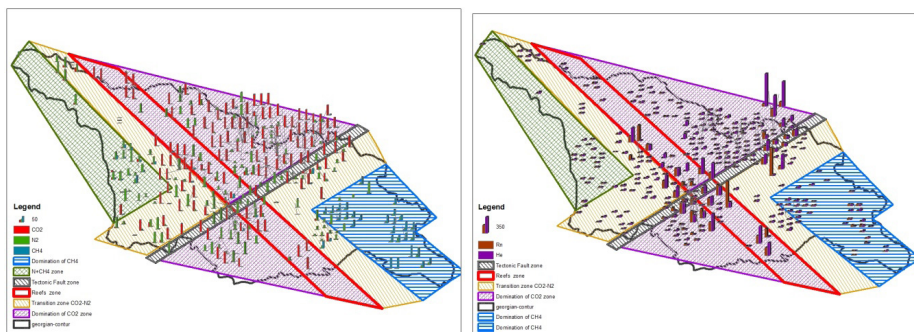


Fig. 9 Natural CO_2 , CH_4 , N_2 (left) and Rn , He (right) gases distribution on the territory of Georgia

Фиг. 9. Разпространение на естествените газове CO_2 , CH_4 , N_2 (вляво) и Rn , He (вдясно) на територията на Грузия

The sediment accumulation processes on the territory of Georgian plate, which is located between Caucasus mountain systems, facilitated the accumulation of biogenic gases (methane, nitrogen, etc.). This is confirmed by the domination of methane in the groundwaters on the lowlands of East Georgia as well as by the existence of oil fields.

There is a different situation on the lowland areas of West Georgia, where the inverse phenomenon is observed. In particular, in the upper Cretaceous age aquifer with low conductivity, the dominant gas is methane, while in the lower Cretaceous age aquifer with relatively high conductivity, we found a nitrogen of an atmospheric origin.

Since the main factor in the distribution of radiogenic radon and helium is the vertical conductivity of rocks and aquifers, they are good indicators for presence of active tectonic faults and lithological „windows”.

For example, on the territory of Georgia, the high values of these gases were observed in Cretaceous limestone series with a good permeability, following the southern slope of Caucasus Mountains as a wide stripe. On the other hand the low values were observed in the closed structures - in the clayey sediments of Georgian Plate. The highest values were observed along the regional tectonic faults and especially on their crossing points.

Conclusion

The natural gases are very sensitive indicators of geological, especially geotectonic state of an area. The distribution of gas associations are strictly connected with the properties of the geological structure of Georgia. The natural gas distribution in the South Caucasus region was investigated as well as the greenhouse gases emissions from natural sources were qualitatively and quantitatively analyzed. It was confirmed that the South Caucasus, particularly Georgia, is rich in mineral springs, characterized by high level of natural gas emissions.

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