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Application of the Data on $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of Carbonates for the Study of Unconventional Reservoirs on the Example of the Bazhenov Source Rocks, Western Siberia, Russia

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Abstract: This paper addresses potential application of data on stable carbon and oxygen isotope composition of carbonates for study of organic rich source rocks on the example of the Late Jurassic–Early Cretaceous Bazhenov Formation (West Siberian petroleum basin, Russia). Geochemical studies were conducted for sections located in central (most productive) and peripheral (northern and southern) regions of the Bazhenov Formation distribution area, containing deposits formed under different conditions. We identified key factors impacting stable isotope composition of carbonate minerals and established relation of their isotope composition to the formation conditions. Using a thermodynamic model of carbon and oxygen isotope exchange in the carbonate–water–carbon dioxide system, it is shown that variations in the isotope composition of secondary carbonates are affected by isotopic composition of primary carbonates in sediments and by the isotope exchange reactions with water and carbon dioxide, generated during the source rocks transformation. Our results demonstrate that stable isotope data for carbonates in the Bazhenov Formation together with standard geochemical methods can be efficiently applied to determine sedimentation conditions and secondary alteration processes of oil source rocks.

Keywords: carbonate mineralization; stable isotopes of carbon and oxygen; the Bazhenov Formation; West Siberian petroleum basin; isotope fractionation; epigenetic transformations; isotope exchange model

1. Introduction

Carbonatization of primary non-carbonate oil source deposits occurs at all stages of their post-sedimentation history. Studies of carbonate minerals allow to determine conditions of formation and secondary alterations of oil source rocks at different stages of lithogenesis, including sedimentation, dia- and catagenesis as well as possible influence of allogeneic fluids [1–7]. Precipitation of carbonate minerals can significantly affect the reservoir, elastic-strength and other properties of the rocks. Relation between reservoir properties, productivity of source deposits and carbonate mineralization has been established in a number of studies [8–15]. Therefore, investigation of carbonatization processes is important for both geological sections characterization and for optimization of development technologies.

Data on oxygen and carbon isotope composition ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$) can significantly complement information obtained by analysis of chemical composition and morphology of carbonate minerals from oil source rocks. Data on the oxygen isotope composition pro-

vide information on genesis of reservoir water as well as on temperatures of carbonatization processes [16–23]. Carbon isotope composition of carbonates depends on the genesis of carbon dioxide involved in carbonates formation [18,22,24–27]. Both carbon and oxygen isotope compositions bring information on ratios of carbonate phases, water and carbon dioxide during processes of carbonatization or recrystallization. The method of clumped isotopes is a useful instrument for evaluation of paleotemperatures from isotope compositions of oxygen and carbon in carbonate minerals, however, it is not widely used for diagenetic settings [28].

Thus, isotope data on carbonate minerals provide information on genesis, formation conditions and potential productivity of unconventional reservoirs. Since interpretation of isotope data is complicated by a significant number of factors affecting oxygen and carbon isotope compositions, such studies should be conducted comprehensively and should take into account all the available data on the considered geological object. In the present work we analyze the potential of methods based on carbon and oxygen isotope compositions of carbonates for study of unconventional reservoirs on the example of the Bazhenov Formation (West Siberian petroleum basin, Russia)—one of the richest petroleum source rocks in the world. The studies were performed for rock samples of three different sections from different parts of the basin, central (most productive) and peripheral (northern and southern), characterized by different sedimentation conditions.

2. Geological Setting

The Bazhenov source rock formation is located in the Western Siberia and covers more than 1 million km² area. The depth of the formation varies from 2.5 to 3.5 km, its thickness is 20–40 m [29–33]. The marine deposits were accumulated under the conditions of the maximum Late Jurassic–Early Cretaceous Sea transgression [32,34–36]. The Bazhenov Formation is highly heterogeneous in its lithology, rock composition and properties. The formation includes a number of lithological members containing siliceous, clayey, carbonate and mixed rock types. The rocks are characterized by high organic matter (OM) content, which varies from 2 to 30 wt. % depending on the location and rock type. Despite more than 50 years of exploration, the Bazhenov Formation is currently one of the most unpredictable geological objects in terms of the field development.

Carbonate minerals within the Bazhenov Formation are represented by calcite, dolomite, and less often by siderite. The primary carbonate material is formed by non-recrystallized shell detritus (bivalves, coccolithophorids, belemnites, ammonites, etc.). Secondary carbonate mineralization is associated with dissolution and redeposition of primary biogenic carbonates in di- and catagenesis and as a result of influence of allogenic fluids [7,33,37–39]. Dolomitization and sideritization processes are more typical for the catagenesis stage [11,38,40] and can also occur under the influence of hydrothermal solutions [41].

In general, the content of carbonate minerals in the Bazhenov Formation is low (from 0.1 wt. % to several wt. %), although there are intervals significantly enriched in carbonate material. The highest carbonate content within the Bazhenov Formation is observed in the central part of the basin and decreases towards the northern and southern parts of the basin [42]. The most abundant carbonate bearing rocks of the Bazhenov Formation are carbonated radiolarites with different calcite/dolomite rates. Carbonate minerals content in these intervals varies first percents: 1–2 wt. % up to 80 wt. %. The rocks may also contain mixed carbonate-clay-siliceous (content of carbonates varies from below 1 wt. % up to 15 wt. %), clay-carbonate-siliceous (15–20 wt. %) and clay-siliceous-carbonate (30–50 wt. %) rocks. Carbonate rich rocks (carbonate content is 70–90 wt. %) are represented by both limestones and dolomitic limestones. They occur in the upper and basal parts of the Bazhenov succession and in the upper part of the underlying succession. Carbonate concretions of different mineral composition are also frequently found in sections of the Bazhenov Formation [43].

In this work we studied carbonated rocks of the Bazhenov Formation from three wells drilled in different parts of the Western Siberia: northern, central and southern (Figure 1). The studies were carried out both for carbonate intervals containing up to 10 wt. % of carbonate carbon and for the rocks with low (less than 1 wt. %) carbonate carbon content. The source deposits in the studied regions were accumulated under different environmental conditions, including marine deepwater settings with a predominance of clay-carbonate-siliceous sedimentation and high content of organic carbon in the central part of the basin, and coastal or transitional conditions with a larger role of terrigenous sedimentation—in the southern and northern parts of the basin.

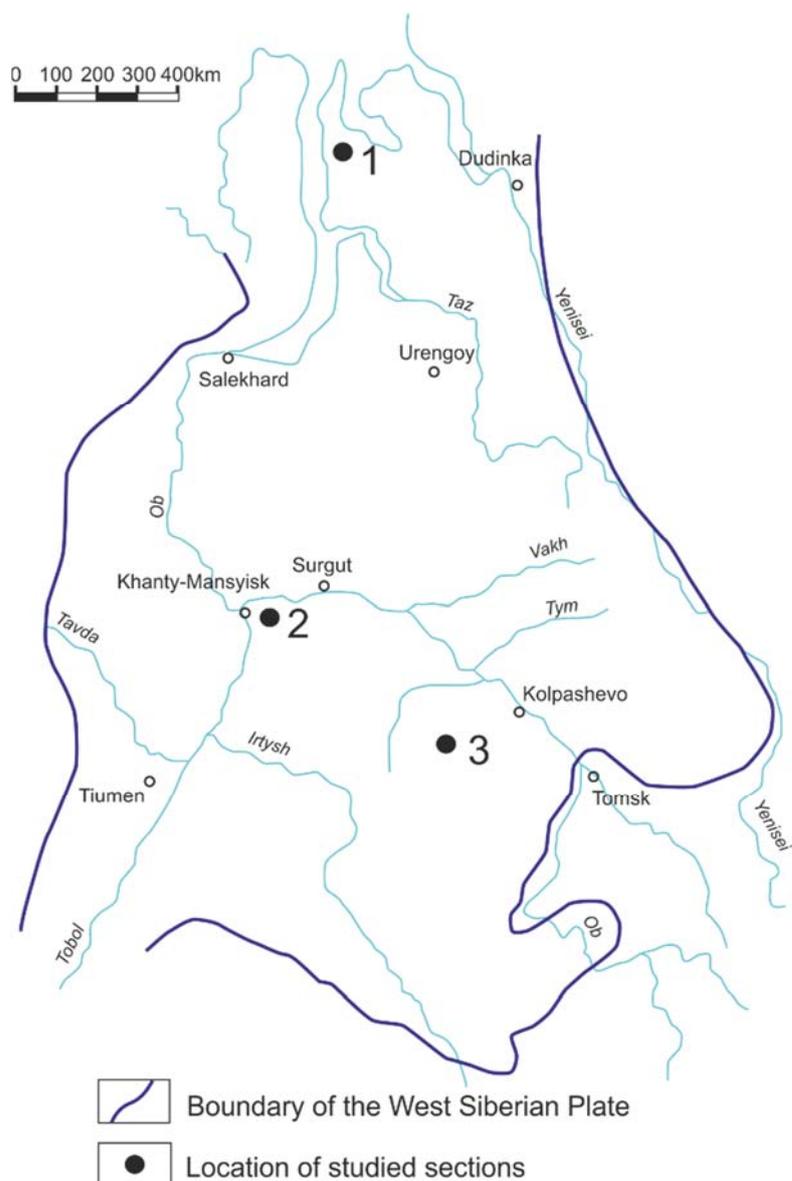


Figure 1. Location of the studied sections (1—northern; 2—central; 3—southern) on the schematic map of the West Siberian Plate.

3. Materials and Methods

For elemental and stable isotope analysis of total carbon, aliquots of rock samples (0.5–5 mg) were placed in tin capsules and analyzed using the EA-IRMS Delta V measuring system; to reduce the error, each sample was analyzed many times. To calibrate the elemental analysis, sulfonamide C₆H₈N₂O₂S was used as a standard with the content of

carbon C 41.84%, nitrogen 16.27%, sulfur 18.62%. To calibrate measurements of stable isotopes composition international standards were used: oil NBS 22, marble IAEA-CO-1, strontium carbonate NBS 23. All results are given in δ values relative to the international VPDB standard for both carbon and oxygen in carbonates; VSMOW standard for oxygen in water. Casein was used as a control sample. Its elemental and stable carbon, nitrogen and sulfur isotope composition were determined during interlaboratory comparative measurements. Accuracy of the isotope composition determination for carbon and oxygen is $\pm 0.2\text{‰}$ and $\pm 0.5\text{‰}$, respectively.

The carbon and oxygen isotope composition of carbonates was analyzed in gaseous CO_2 obtained by chemical decomposition of carbonates with 100% orthophosphoric acid. Powdered rock samples (approximately 0.3 g) were placed in 20 mL head-space vials together with a short glass tubes containing 1g of 100% orthophosphoric acid in a solid state, capped with a crimper and flashed through a syringe needle for 1 h with helium to remove air from the vials. After removing the needle, the vials were heated until the acid became liquid. Afterwards, the vials were turned over to mix samples with the acid. Carbonate minerals present in rock samples reacted with phosphoric acid for 24 h at a temperature of 25 °C; the released CO_2 was sampled automatically using DANI HSS 86.50 autosampler (DANI Colongo Monzese, Italy) coupled with Delta V isotope ratio mass spectrometer (Thermo Scientific, Bremen, Germany).

The acid solution was filtered from the rock samples remaining in the vials. The samples were repeatedly washed with distilled water, dried in a desiccator at 50 °C and analyzed two or more times using the EA-IRMS Delta V measuring system to obtain data on the organic carbon stable isotope composition. Thus, for the studied samples we obtained the data on the total content and isotope composition of mixed organic and carbonate carbon before acid treatment, the data on the content and isotope composition of the organic carbon and the data on the isotope composition and content of carbonate carbon after acid treatment. Using the results of measurements of the organic and carbonate carbon stable isotope composition and the isotope balance Equation (1), the contents of carbonate and organic carbon were calculated with more precision.

Pyrolytic studies were performed on the same samples, using Rock-Eval method [44] on a HAWK RW device from Wildcat Technologies. A standard for source rocks bulk rock technique was used: two-stage stepwise heating of a rock sample in an inert medium (helium) and an air flow up to temperature of 850 °C. During the heating hydrocarbons (flame ionization detector), CO and CO_2 (infrared detector cells) are detected. The output pyrolytic parameters are S1 (gaseous and light petroleum hydrocarbons) and S2 (products of kerogen pyrolysis and heavy hydrocarbons fraction) measured in mg HC/g rock, as well as parameters S3 (the amount of CO_2 released during the pyrolysis), S4 (the amount of CO_2 released during the oxidation) and S5 (the amount of CO_2 released during the carbonate decomposition) measured in mg CO_2 /g rock. These parameters are used for the calculation of the total organic carbon content TOC in wt. %. The temperature of the maximum of peak S2 is T_{max} , which is an indicator of the maturity. Processing of the obtained data included calculation of hydrogen index $\text{HI} = \text{S}_2/\text{TOC} \times 100$, oxygen index $\text{OI} = \text{S}_3/\text{TOC} \times 100$, productivity index $\text{PI} = (\text{S}_1)/(\text{S}_1 + \text{S}_2)$ and other pyrolytic parameters. To exclude the influence of heavy hydrocarbons during maturity estimates, pyrolysis of rocks before and after extraction was performed [45,46].

4. Results and Discussion

The studied wells are shown in Figure 2. The depths are shown as distance from the bottom of the Bazhenov Formation. The bottom of the formation is located at depth of 3100 m in the central, 3450 m in the northern and 2650 m in the southern sections.

The central section has thickness of 40 m and is presented by kerogen-rich clay-siliceous and clay-carbonate-siliceous rocks (Figure 2). Isotopic studies were conducted for 14 samples characterized by different carbonate content, including: (1) carbonate rich

rocks from different parts of the section (kerogen-clay-siliceous-carbonate rocks with different ratios of rock-forming components with carbonate carbon content of 4.7–9.2%); (2) carbonated kerogen-clay-siliceous rocks with carbonate carbon content less than 2% (Table 1).

The southern section has a thickness of 24 m and is presented by clay-siliceous rocks with carbonate carbon content of up to 1%. Isotope studies were conducted for nine samples (Table 1).

In the northern section (thickness 20 m), carbonate-rich rocks are present in the lower part (sideritized clay-siliceous rocks) and in the upper part (calcitated radiolarite), with carbonate carbon content of 8 and 10%, respectively. Samples from the middle part of the section are presented by weakly carbonated (less than 1% carbonate carbon content) siliceous-clay, clay-siliceous and clay rocks. In total, 18 samples of both carbonate-rich and weakly carbonated (carbonate carbon content less than 1%) rocks were studied from the northern section (Table 1).

For the selected samples we determined the organic and carbonate carbon content (C_{org} , C_{carb}), the carbon and oxygen isotope compositions ($\delta^{13}C$, $\delta^{18}O$) of carbonates, as well as the organic carbon isotope composition ($\delta^{13}C_{org}$). The obtained data are given in Table 1 and illustrated in Figure 2.

Table 1. Results of geochemical analysis for three sections: organic and carbonate carbon content, isotopic composition of C_{org} , C_{carb} , and O_{carb} , and pyrolysis data.

Central Section											
Formation	Depth from the Bottom of the Bazhenov Formation	Lithological Type of Rocks	C_{or} , g, %	C_{car} , b, %	$\delta^{13}C_{org}$, ‰	$\delta^{13}C_{carb}$, ‰	$\delta^{18}O_{carb}$, ‰	T_{max} , °C	HI, mg HC/g C_{org}	OI, mg CO_2 /g C_{org}	PI
Bazhenov	39.38	Kerogen-clay-siliceous-carbonate	6.7	8.4	−30.3	−13.9	−2.6	445	325	8	0.14
	38.62	Kerogen-clay-siliceous-carbonate	5.8	8.0	−30.5	−15.8	0.8	447	335	10	0.15
	38.52	Kerogen-clay-siliceous-carbonate	5.4	8.6	−30.5	−13.8	−4.5	444	306	3	0.13
	36.44	Kerogen-clay-siliceous	17.2	1.5	−30.8	−6.3	−7.2	446	331	2	0.1
	29.53	Kerogen-clay-siliceous-carbonate	4.3	9.2	−31.1	2.0	−7.3	439	304	25	0.19
	29.49	Kerogen-clay-siliceous-carbonate	4.4	8.6	−31.0	2.3	−8.4	442	300	9	0.23
	22.45	Kerogen-clay-siliceous	9.1	0.1	−31.2	−4.2	−10.3	439	256	3	0.27
	18.66	Kerogen-clay-siliceous	7.9	2.4	−31.2	−8.1	−12.0	443	296	9	0.17
	18.15	Kerogen-clay-siliceous	4.9	0.2	−31.2	−10.9	−16.2	443	281	6	0.3
	11.03	Clay-kerogen-siliceous-carbonate	3.8	8.3	−29.8	−2.4	−9.8	440	283	15	0.28
	8.39	Clay-kerogen-siliceous	9.5	0.4	−30.7	−0.5	−15.9	448	287	2	0.23
	8.18	Kerogen-clay-siliceous	8.7	0.4	−30.8	−6.9	−12.4	447	302	2	0.24
	5.94	Kerogen-clay-siliceous	9.3	0.6	−31.0	−9.8	−15.1	449	314	5	0.22
5.27	Kerogen-clay-carbonate-siliceous	4.6	4.7	−30.6	0.9	−9.3	446	362	3	0.29	
Northern Section											

Formation	Depth from the Bottom of Bazhenov Formation	Lithological Type of Rocks	Cor g%	Ccar b. %	$\delta^{13}\text{Cor}$ g ‰	$\delta^{13}\text{Cca}$ rb ‰	$\delta^{18}\text{Oc}$ arb ‰	Tmax, °C	HI, mg HC/g Corg	OI, mg CO ₂ /g Corg	PI
Bazhenov	18.7	Siliceous-carbonate	1.9	9.9	-30.7	-26	-0.3	438	205	37	0.13
	18.24	Siliceous-clay	4.6	0.1	-31.1	-12.9	-9.6	439	247	7	0.20
	17.31	Siliceous-clay	3.4	0.2	-30.4	-1.5	-5.4	433	100	18	0.35
	17.03	Siliceous-clay	2.4	0.1	-30.7	-11.2	-11.4	442	279	12	0.13
	15.79	Siliceous-clay	2.8	0.1	-30.0	-12.0	-11.3	434	114	13	0.39
	15.32	Siliceous-clay	4.3	5.1	-32.4	-5.5	-7.5	439	479	3	0.07
	15.07	Kerogen-siliceous-clay	8.8	0.4	-32.2	-11.8	-10.1	440	358	5	0.11
	14.76	Kerogen-siliceous-clay	8.1	0.2	-32.4	-14	-13.3	442	511	2	0.09
	14.47	Kerogen-siliceous-clay	7.6	0.0	-31.4	-13.9	-13.8	437	409	3	0.09
	13.9	Siliceous-clay	1.0	0.2	-29.5	-14.1	-12.1	435	75	28	0.48
	12.72	Kerogen-siliceous-clay	9.5	0.3	-31.6	-10.5	-8.4	437	406	3	0.10
	11	Siliceous-clay	2.1	0.2	-29.8	-16.6	-13.6	436	140	3	0.10
	9.28	Kerogen-siliceous-clay	7.8	0.1	-31.5	-15.5	-12.1	439	369	3	0.13
	8.4	Siliceous-clay	6	0.5	-32.1	-15.6	-13.1	441	406	5	0.09
6.73	Kerogen-siliceous-clay	11.1	0.3	-31.5	-15.1	-12.6	437	394	18	0.34	
Abalak	5.14	Carbonated-clay	1.5	0.4	-28.5	-15.9	-10.7	436	68	12	0.17
	3.46	Siliceous-clay	2.6	0.3	-29.8	-15.3	-12.2	439	204	108	0.28
	0.05	Clay-siliceous-siderite	0.6	8.1	-28.5	-10.8	-1.2	433	51	9	0.32

Southern section

Formation	Depth from the bottom of Bazhenov Formation	Lithological Type of Rocks	Cor g%	Ccar b. %	$\delta^{13}\text{Cor}$ g ‰	$\delta^{13}\text{Cca}$ rb ‰	$\delta^{18}\text{Oc}$ arb ‰	Tmax, °C	HI, mg HC/g Corg	OI, mg CO ₂ /g Corg	PI
Bazhenov	29.44	Siliceous-clay	6.4	0.9	-30.9	-17.1	-17.4	428	564	6	0.03
	21.44	Siliceous-clay	9.0	0.2	-31.6	-8.3	-17.5	426	703	3	0.03
	21.24	Siliceous-clay	7.0	0.4	-31.9	-8.5	-17.5	427	693	2	0.03
	17.54	Clay-siliceous	10.4	1.0	-31.5	-16.1	-18.5	423	742	2	0.03
	16.44	Clay-siliceous	7.9	0.1	-31.5	-10.5	-18.9	430	698	3	0.03
	14.44	Clay-siliceous	11.9	0.4	-31.6	-6.9	-19.2	423	707	–	–
	14.04	Clay-siliceous	10.6	0.4	-31.7	-6.9	-16.7	431	760	2	0.03
	13.34	Clay-siliceous	10.6	0.3	-31.8	-5.4	-15.9	429	738	2	0.02
	9.44	Clay-siliceous	11.1	0.4	-31	-5.1	-15.3	427	732	3	0.03

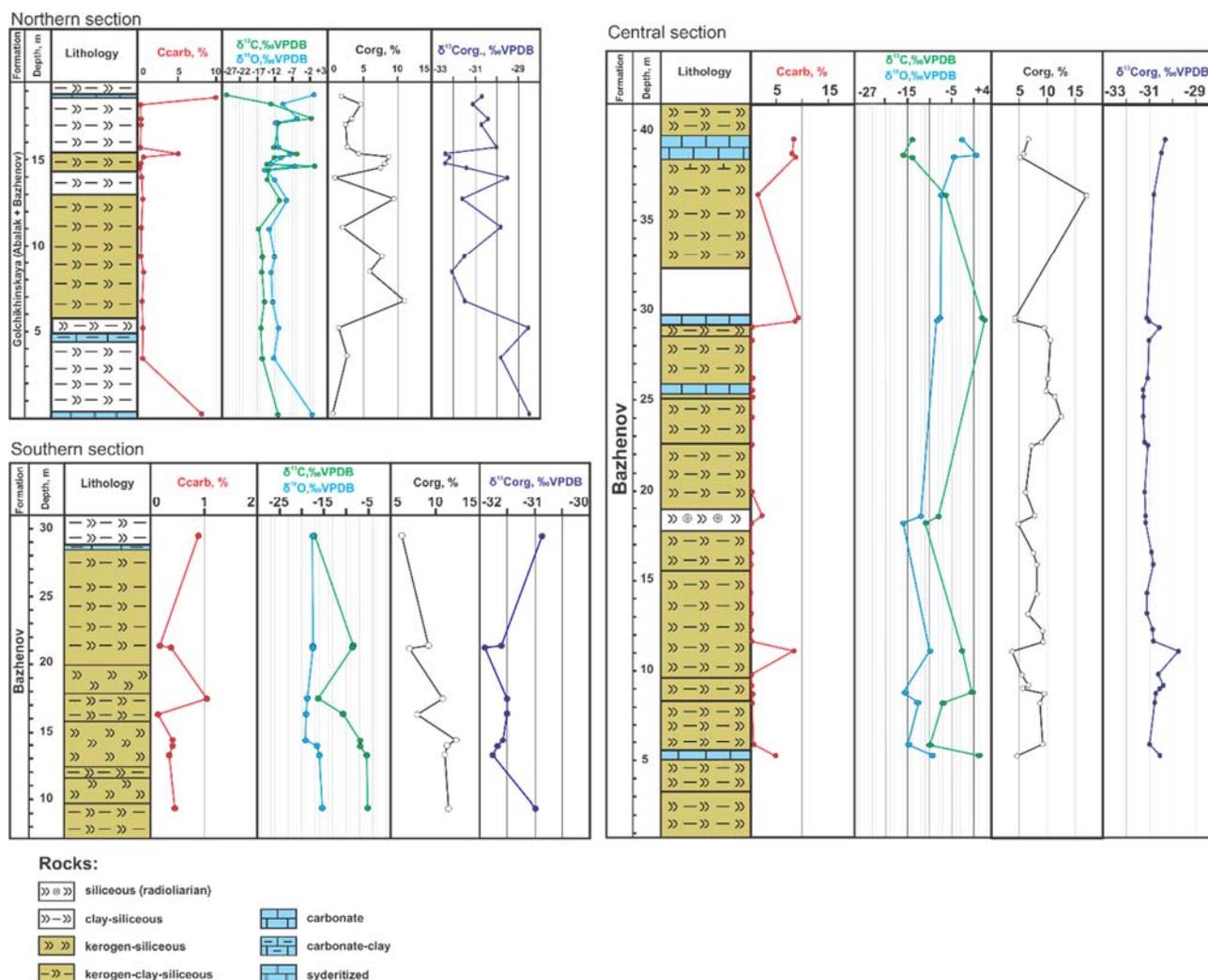


Figure 2. Studied sections of the Bazhenov Formation and upper part of underlying sediments with data on the organic and carbonate carbon content and isotopic characteristics. Depths are shown as distance from the bottom of the Bazhenov Formation.

As follows from Table 1 and Figure 2, the carbon and oxygen isotope composition in carbonate minerals varies considerably within the studied sections: $\delta^{18}\text{O}$ varies from -19.2 to $+0.8\text{‰VPDB}$, $\delta^{13}\text{C}$ takes values from -26 to $+2.3\text{‰VPDB}$. No clear correlation of the carbonate isotope composition, carbonate content and organic matter content or organic matter carbon isotope composition is observed in the studied sections. For a number of intervals positive correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ is observed, while for others negative correlation is detected. Simultaneous shift of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ towards smaller values indicates the processes of dissolution and redeposition of primary marine carbonates accompanied by changes in the pore waters pH and temperature increase during dia- and catagenesis and larger role of isotopically light CO_2 from OM and/or hydrocarbons (HC). The $\delta^{13}\text{C}$ shift towards larger values accompanied by $\delta^{18}\text{O}$ decrease indicates decreasing role of CO_2 from OM and predominance of CO_2 formed during dissolution of the biogenic marine carbonates.

The $\delta^{13}\text{C}-\delta^{18}\text{O}$ diagram, shown in Figure 3, allows to distinguish and classify groups of carbonates by genesis and conditions of formation. The diagram presents the data on carbon and oxygen isotope composition of the studied samples as well as the published data on isotope composition of carbonates from the Bazhenov Formation and the upper part of underlying Abalak Formation in the central part of the West Siberian petroleum basin.

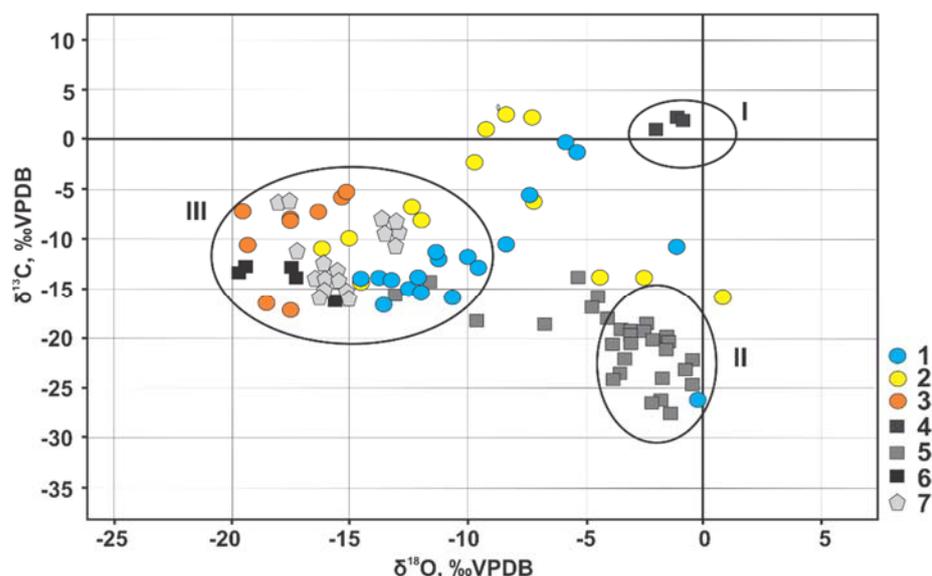


Figure 3. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the studied carbonate rocks of the Bazhenov Formation. 1—carbonate and carbonated siliceous-clay rocks, northern section; 2—carbonate-kerogen-clay-siliceous rocks, central section; 3—weakly carbonated clay-siliceous rocks, southern section; 4—belemnites, Abalak Formation [47]; 5—limestones, top of the Abalak Formation [7,47]; 6—vein calcite in limestones, top of the Abalak Formation [7]; 7—carbonated rocks of the Bazhenov Formation [47]. 4–7—samples from the central part of the Bazhenov Formation distribution area. I–III—genetic groups of carbonates: I—primary biogenic; II—sedimentary-diagenetic methane-derived; III—secondary catagenetic.

Group I shown in the diagram includes points with values of $0 \pm 4\text{‰VPDB}$ for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, corresponding to primary biogenic limestones or shell remains [47], which is also consistent with the data reported in [18–21]. Not a single sample from the studied sections fell into Group I.

Group II includes points with $\delta^{13}\text{C}$ values less than -15‰VPDB and $\delta^{18}\text{O}$ values above -5‰VPDB . According to [7,47], this group corresponds to sedimentary-diagenetic methane-derived limestones. These carbonates are formed on the seabed in the areas of focused methane discharge, when methane reaching the seafloor surface is oxidized by microorganisms under anaerobic conditions. Due to bacterial reworking of the isotopically light methane, the carbon dioxide and carbonates which are formed with participation of this carbon dioxide are considerably depleted in ^{13}C [47–52]. Since the process generally occurs in the upper part of marine sediments, $\delta^{18}\text{O}$ of methane-derived carbonates is close to normal marine biogenic ones. Among the samples studied in this work, only one sample with the highest carbonate carbon content from the upper part of the Bazhenov Formation of the northern section ($\delta^{13}\text{C} -26\text{‰VPDB}$) can be attributed to carbonates of this type (group II). In the studied collection there are several samples, which have isotope composition close to group II carbonates, including one sample from the northern section ($\delta^{13}\text{C} -12.9\text{‰VPDB}$) and three samples from the central section ($\delta^{13}\text{C}$ from -15.8 to -13.8‰VPDB). The low $\delta^{13}\text{C}$ values indicate the high amount of ^{13}C -depleted CO_2 , which could be also formed during the OM transformation in catagenesis.

Most of the studied samples belong to group III, which is characterized by $\delta^{13}\text{C}$ values from -17.1 to -5‰VPDB and $\delta^{18}\text{O}$ values from -19.2 to -9‰VPDB . A significant shift in the carbon and oxygen isotope composition towards smaller values for the samples of group III is associated with their formation or recrystallization under conditions of elevated temperatures in the presence of formation water of marine genesis, as well as isotopically light carbon dioxide formed during the OM and HC transformation in catagenesis. Secondary carbonates of group III are common for the Bazhenov Formation and are also characteristic for calcite veins in limestones in the upper part of the Abalak Formation [7,38,47].

We also note the presence of samples with intermediate values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. Between groups I and III we find “diagenetic” carbonates formed under conditions similar to those of group III, but at temperatures below 60 °C.

Therefore, most of the carbonated rocks of the studied sections fall into group III—secondary carbonates. Their isotope composition was formed at elevated temperatures during interaction with formation water and isotopically light carbon dioxide formed during the OM transformation. Reservoir water in marine source rocks is of marine genesis. Content of water in sediments decreases from 10% at the initial stage of diagenesis to values less than 1% at the catagenesis stage.

The CO_2 presence is associated with two processes. The first one is aerobic oxidation of OM and bacterial sulfate reduction during diagenesis. According to the reaction of sulfate reduction with a sulfate content in water of 2700 mg/L, its complete reduction can lead to the formation of up to 2.5 g/L of CO_2 in the system. In oxidizing environment, in the upper layers of sediments, an important role is played by the reaction of aerobic oxidation of organic carbon by oxygen dissolved in water, as well as by oxygen of Fe and Mn oxides, leading to CO_2 production [53]. However, the actual CO_2 content in pore waters of modern marine sediments is significantly lower than the calculated value and usually does not exceed 1 g/L [54–57]. The reason is probably the precipitation of carbonate minerals at higher CO_2 concentrations due to over-saturation in respect to calcite and dolomite. According to [58], especially in pore water of siliciclastic sediments, by extensive sulfate reduction the increase in carbonate alkalinity outweighs the decrease in pH, and therefore prevents dissolution and enhances formation of carbonates in diagenesis. The second, more significant factor of the CO_2 formation is elimination of the oxygen-containing radicals of OM with increasing reservoir temperatures, which is reflected by a decreasing oxygen content in OM. The amount of CO_2 that can be released from OM is associated with the difference in the oxygen content in kerogen at different stages of catagenesis. According to [59], increasing maturity of OM in the Bazhenov Formation rocks is associated with the decreasing oxygen content in kerogen from 12 to 5%, together with decreasing water content, suggesting a significant increase of the CO_2 concentration in fluids. Roughly estimated, the maturation of 1 kg rock with kerogen content of 5% can release total amount of CO_2 about 5g. Taking into account low water content from about 20% at the beginning of catagenesis to 1–2% at late stages [60] the produced fluids should have CO_2 content above 20 g/L. This high value is calculated from total CO_2 and water release during millions of years. Instantaneous CO_2 content was probably lower but still high enough to be over-saturated in respect to carbonates and provide calcite and dolomite formation.

The direction and amplitude of oxygen and carbon isotope variations can be considered in a frame of the model describing isotope interaction in a carbonate–water–carbon dioxide system. Below we consider a thermodynamic model that describes isotope exchange between the components of the system at given ratios, temperatures and known coefficients of isotopic fractionation between phases. Simulations were performed using isotope balance Equations (1) and (2) for oxygen and carbon, which relate the initial isotopic composition of carbonate (i) and isotopic composition after exchange (f) with the content of H_2O , CaCO_3 ($\text{H}_2\text{O}/\text{CaCO}_3$) and total CO_2 in the fluid (sum of all forms of carbon dioxide— CO_2 , HCO_3^- , and CO_3^{2-}), recorded as molar fractions of oxygen $X_{\text{O-CO}_2}$, $X_{\text{O-CaCO}_3}$, $X_{\text{O-H}_2\text{O}}$ and carbon $X_{\text{C-CaCO}_3}$ and $X_{\text{C-CO}_2}$. The simulations are also based on the relations between the coefficients of oxygen and carbon isotope fractionation between phases and the temperature T (Kelvin), taken from [61], [62] and [63] (Equations (3)–(6)).

$$\delta^{18}\text{O}_{\text{CaCO}_3} \cdot X_{\text{O-CaCO}_3} + \delta^{18}\text{O}_{\text{CO}_2} \cdot X_{\text{O-CO}_2} + \delta^{18}\text{O}_{\text{CO}_2} \cdot X_{\text{O-H}_2\text{O}} = \delta^{18}\text{O}_{\text{CaCO}_3} \cdot X_{\text{O-CaCO}_3} + \delta^{18}\text{O}_{\text{CO}_2} \cdot X_{\text{O-CO}_2} + \delta^{18}\text{O}_{\text{H}_2\text{O}} \cdot X_{\text{O-H}_2\text{O}} \quad (1)$$

$$\delta^{13}\text{C}_{\text{CaCO}_3} \cdot X_{\text{C-CaCO}_3} + \delta^{13}\text{C}_{\text{CO}_2} \cdot X_{\text{C-CO}_2} = \delta^{13}\text{C}_{\text{CaCO}_3} \cdot X_{\text{C-CaCO}_3} + \delta^{13}\text{C}_{\text{CO}_2} \cdot X_{\text{C-CO}_2} \quad (2)$$

$$\Delta^{18}\text{O}_{\text{CaCO}_3\text{-H}_2\text{O}} = \delta^{18}\text{O}^f_{\text{CaCO}_3} - \delta^{18}\text{O}^f_{\text{H}_2\text{O}} = 2.78 \cdot 10^6 / (T)^2 - 2.89 \quad (3)$$

$$\Delta^{18}\text{O}_{\text{CaCO}_3\text{-CO}_2} = \delta^{13}\text{C}^f_{\text{CaCO}_3} - \delta^{13}\text{C}^f_{\text{CO}_2} = 1.71 \cdot 10^6 / (T)^2 - 10.01 \cdot 10^3 / (T) + 3.45 \quad (4)$$

$$\Delta^{18}\text{O}_{\text{CO}_2\text{-H}_2\text{O}} = \delta^{18}\text{O}^f_{\text{CO}_2} - \delta^{18}\text{O}^f_{\text{H}_2\text{O}} = 2.3 \cdot 10^6 / (T)^2 + 5.34 \cdot 10^3 / (T) - 3.51 \quad (5)$$

$$\Delta^{13}\text{C}_{\text{CaCO}_3\text{-CO}_2} = \delta^{18}\text{O}^f_{\text{CO}_2} - \delta^{18}\text{O}^f_{\text{CaCO}_3} = 2.4 \cdot 10^6 / (T)^2 - 4.92 \cdot 10^3 / (T) - 0.44 \quad (6)$$

Although the considered model is simplified, it describes and illustrates general trends in the changes of isotope compositions of oxygen and carbon in carbonates resulting from their isotope interaction with water and carbon dioxide in rock forming processes. Below we consider an example of simulation of the isotope composition in the calcite–water–CO₂ system at different interaction temperatures. The calcite content is set equal to 0.5 wt. % in the rocks, its initial isotope composition is set to $\delta^{13}\text{C} = +2\text{‰}$ and $\delta^{18}\text{O} = -0.1\text{‰}$ VPDB, which corresponds to the average values for primary carbonates in the Bazhenov Formation. The water content in this example is set equal to 10 wt. %, the oxygen isotope composition of water is set to $\delta^{18}\text{O} = -1\text{‰}$ VSMOW, corresponding to the value calculated from $\delta^{18}\text{O}$ of unchanged belemnites rostras from the Bazhenov Formation and underlying deposits [47]. The CO₂ content in water (the sum of all forms of carbon dioxide) takes a wide range of values from 0.00048 to 0.12 mol/kg. The carbon isotope composition of the initial CO₂ is set to $\delta^{13}\text{C} = -31\text{‰}$, which corresponds to the isotopic composition of the Bazhenov Formation OM. Assuming that biogenic carbon dioxide is mainly a product of OM decarboxylation reactions at elevated temperatures, the initial oxygen isotope composition of CO₂ was considered to be similar to the average value of marine plants with $\delta^{18}\text{O} = +27\text{‰}$ VSMOW [64].

The results of simulation of calcite isotope composition at different temperatures and CO₂ content are shown in Figure 4 together with $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values obtained for the rocks from the three studied sections. As follows from this simulation example, a temperature increase leads to the formation of ¹⁸O depleted carbonates. While marine carbonates are characterized by $\delta^{18}\text{O}$ value of about 0‰ VPDB, re-equilibration with formation water of oceanic genesis leads to depletion in ¹⁸O up to $\delta^{18}\text{O}$ values less than -13‰ at the temperature of about 100 °C. If the CO₂ content in the system is about 0.12 mol/kg of rock, temperature increase shifts the initial value of the carbon isotope composition of marine carbonates from 0 ‰ VPDB to the values below -14‰ VPDB.

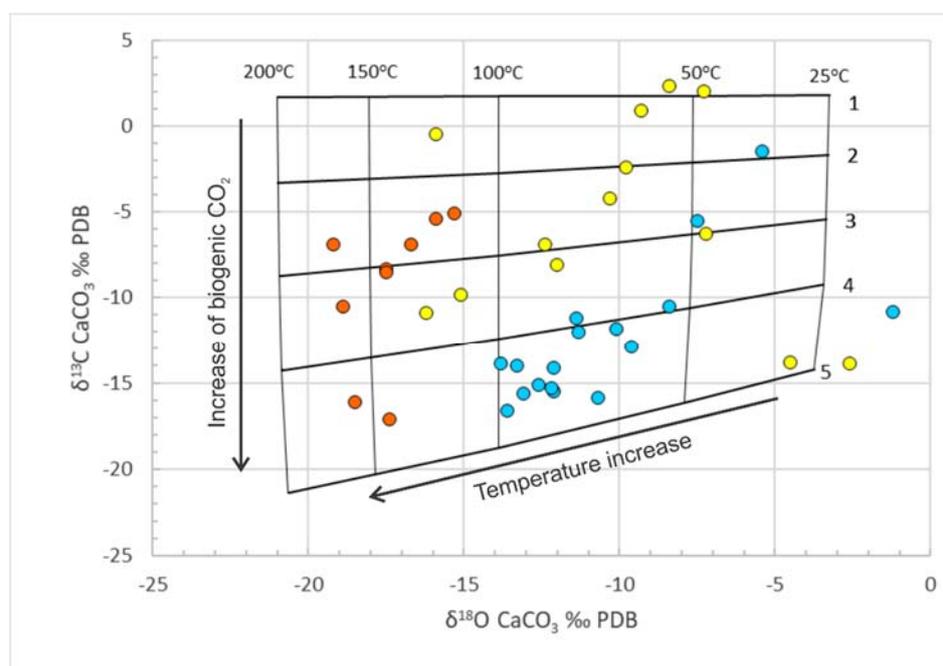


Figure 4. Oxygen and carbon isotope composition of carbonates from the studied sections (northern—blue; central—yellow; southern—orange circles). Lines indicate the equilibrium values of the carbon and oxygen isotope composition of calcite in the rocks containing calcite (0.05 mol/kg of rock), water (5.6 mol/kg of rock) and CO₂ (1—0.00048 mol/kg of rock; 2—0.0096 mol/kg of rock; 3—0.024 mol/kg of rock; 4—0.048 mol/kg of rock; 5—0.12 mol/kg of rock) in the temperature range from 25 to 200 °C. Initial values of δ¹³C and δ¹⁸O: δ¹³C_{CO₂} = −31‰ VPDB; δ¹⁸O_{water} = −1‰ VSMOW; δ¹³C_{calcite} = +2‰ VPDB and δ¹⁸O_{calcite} = −0.1‰ VPDB.

Using the constructed diagram, we can draw a number of conclusions regarding the temperatures at which carbonatization occurred. Indeed, the carbonate-rich samples from wells in the northern and central parts of the basin are characterized by the highest δ¹⁸O values typical for sedimentary carbonates deposited in equilibrium with seawater at temperatures below 25 °C. Low δ¹³C values of these samples indicate participation of isotopically light CO₂ in carbonates formation, including CO₂ formed as a result of anaerobic oxidation of methane at the stage of sedimentation and early diagenesis (the lowest δ¹³C values in Figure 4 correspond to group II in Figure 3). For the rest of samples from these sections, a decrease of ¹³C isotope content with decreasing ¹⁸O content is observed. The δ¹³C and δ¹⁸O values lower than those characteristic for marine biogenic carbonates indicate that the carbonate material is secondary, precipitated at elevated temperatures (group III in Figure 3). Comparison to the simulation results suggests an increase in the relative content of biogenic CO₂ with increasing fluid temperature to 100 °C in the northern part, and to 125 °C in the central part of the basin.

The location of points corresponding to the samples from the southern section in the diagram shown in Figure 4 indicates significant concentrations of biogenic carbon dioxide in fluids and an elevated temperature of carbonates deposition from 110 to 165 °C. However, the conclusion about elevated temperatures does not agree with the results of pyrolysis data. According to Rock-Eval analysis, the samples are characterized by the values of T_{max} (423–429 °C) corresponding to immature kerogen (Table 1) and by the highest values of the hydrogen index (HI), which is clearly visible in the modified Van Krevelen diagram (Figure 5a) and plot showing PI versus T_{max} after [65] (Figure 5b). Pyrolytic data indicate that, in contrast to the carbonate isotope data, the formation temperatures of the rocks from the southern section were lower than in the central and northern regions.

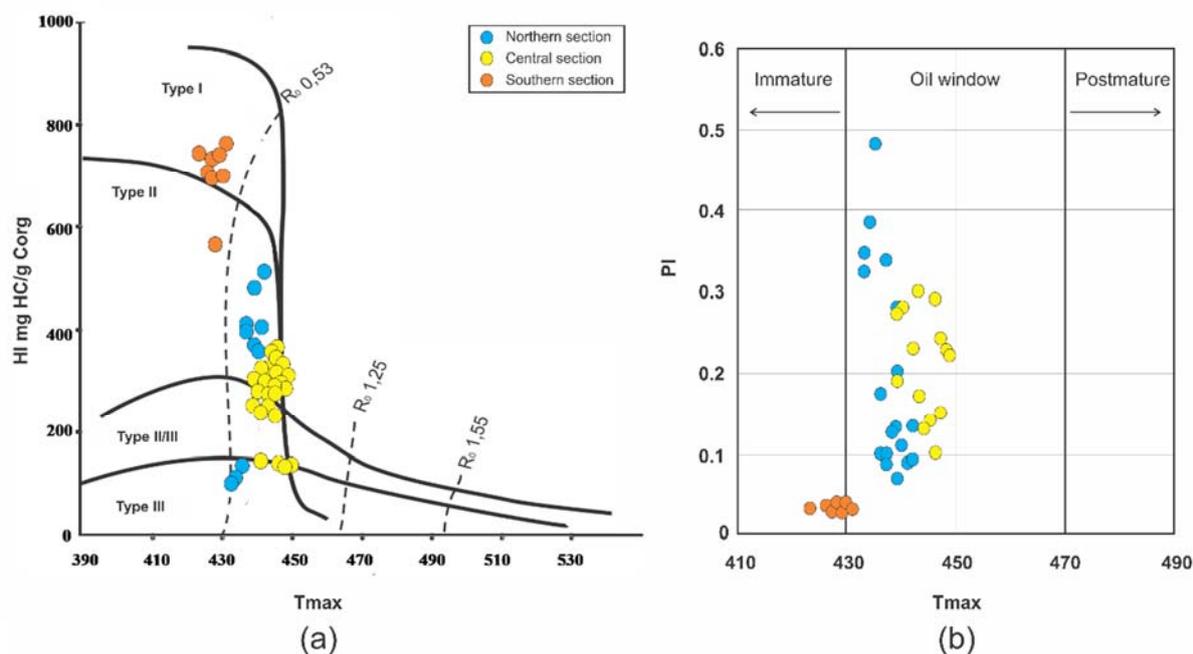


Figure 5. Pyrolysis data: (a) modified Van Krevelen diagram; (b) plot of production index ($S1/(S1 + S2)$) versus T_{max} (°C).

Low values of the carbonates oxygen isotope composition can be possibly explained by the decreased seawater $\delta^{18}\text{O}$ in the southern part of the basin. We should note that in the simulations used for Figure 4 construction the oxygen isotope composition of water was assumed to be close to that of ocean water ($\delta^{18}\text{O} = -1\text{‰ VSMOW}$). If the initial oxygen isotope composition of water from the southern part of the region was lower as a result of river run-off, then the values of $\delta^{18}\text{O}$ in carbonates would be close to those observed at lower reservoir temperatures. According to the lithological and paleontological data, Bazhenov paleobasin is considered as marine, but sedimentation conditions were not the same in different parts of the basin and varied from typically marine in the central part to coastal marine in the marginal zones [34]. As a result, ratios of waters of different genesis vary in different parts of the basin. The $\delta^{18}\text{O}$ values observed in the waters of modern inland and marginal seas and lagoons are controlled by the ratio of seawater and river discharge and can vary in a wide range, reaching $\delta^{18}\text{O}$ values as low as -5‰ – -10‰ VSMOW in desalinated areas [66–71].

Taking into account the possible variations in the isotope composition of seawater, we modified the initial model parameters including oxygen isotope composition of seawater and primary carbonates in order to interpret the data on the $\delta^{18}\text{O}$ of carbonates in the southern section. We set $\delta^{18}\text{O}$ of water equal to -6‰ VSMOW and isotope values for primary calcite: $\delta^{18}\text{O}$ equal to -4.9‰ and $\delta^{13}\text{C}$ equal to -3‰ VPDB . Results of the simulations are given in Figure 6.

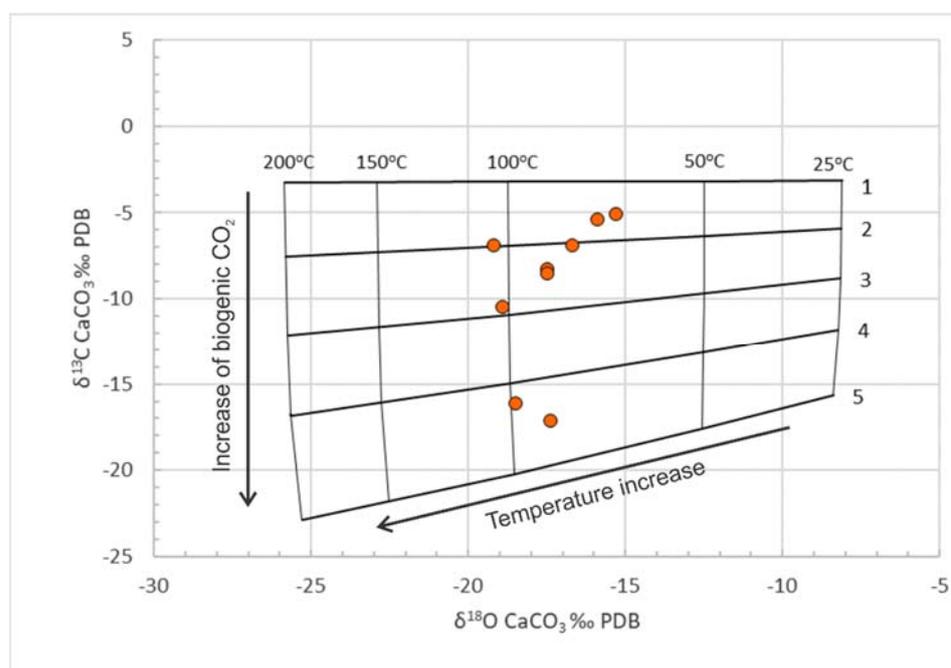


Figure 6. Oxygen and carbon isotope composition of carbonates from the southern section. Lines indicate the equilibrium values of the carbon and oxygen isotopes composition of calcite in the rocks containing calcite (0.05 mol/kg of rock), water of mixed genesis (5.6 mol/kg of rock), and CO₂ of organic genesis (1–0.00048 mol/kg of rock; 2–0.0096 mol/kg of rock; 3–0.024 mol/kg of rock; 4–0.048 mol/kg of rock; 5–0.12 mol/kg of rock) in the temperature range from 25 to 200 °C. Initial values of δ¹³C and δ¹⁸O: δ¹³C_{CO₂} = −31‰ VPDB; δ¹⁸O_{water} = −6‰ VSMOW; δ¹³C_{calcite} = −3‰ VPDB and δ¹⁸O_{calcite} = −4.9‰ VPDB.

Correction of the initial values of water and carbonates oxygen isotope composition leads to a shift in the simulated lines to the area of lower temperature values. In the diagram (Figure 6) the measured values of the carbonates' isotope composition fall into the area corresponding to the interaction temperatures of 70–105 °C, which is in much better agreement with low maturity of OM, indicated by the pyrolytic studies. Thus, according to the data for the southern section, we can conclude that this part of the Bazhenov Sea was significantly (about 30%) depleted in ¹⁸O by river run-off during the sedimentation process.

5. Conclusions

In the current study we analyzed the relation between isotope composition of oxygen and carbon in carbonates and the conditions of oil source rocks formation and transformation on the example of the Bazhenov Formation. The studies were performed for three sections of the Bazhenov Formation located in the central, southern and northern regions of the West Siberian petroleum basin using previously published data on this geological object.

According to the stable isotope composition we identified three main groups of carbonate minerals different in genesis and formation conditions. The first group includes primary carbonate minerals formed from the shells of marine organisms, isotope composition of which varies in the range from −4 to +4‰ VPDB for oxygen and carbon. The second group includes carbonates formed as a result of bacterial anaerobic oxidation of methane in the areas of increased methane content in marine sediments. This group is characterized by abnormally low values of carbon isotope composition and values of oxygen isotope composition, close to those in normal marine biogenic carbonates. The third group includes carbonates transformed in the zones of elevated reservoir temperatures as a result of interaction with reservoir fluids. They are characterized by lower values of both carbon and oxygen isotope composition compared to the primary marine carbonates.

We analyzed the relation of the carbonate isotope composition with the temperature of carbonatization processes and composition of the reservoir fluid using a thermodynamic model of the isotopic interaction of carbonates with the fluid containing water of marine origin and biogenic carbon dioxide. It was shown that the values of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ decrease with increasing temperature, and with increase of water and carbon dioxide content with respect to the carbonate content. At the same time, a significant decrease in $\delta^{18}\text{O}$ values of carbonates result from the sea water dilution by the river discharge.

The performed analysis of the isotopic data on carbonates of the Bazhenov Formation complements existing knowledge about the processes and factors controlling the oxygen and carbon isotope composition of carbonate minerals. Obtained results could be applied in the study of conditions of source rock formations based on isotope composition of carbonate minerals, required for unconventional reservoir characterization and basin modeling.

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