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Carbon Isotope Composition of Sedimentary Rocks in the Southern Siberian Platform and Surrounding Fold Systems

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Abstract—Organic carbon isotope composition was studied in the sedimentary cover of the southern Siberian Platform and its surrounding fold systems. The rocks experienced catagenesis, metamorphism, and metasomatism. The chloroform bitumoid (CB) has a stable carbon isotope composition within a wide range of postsedimentation transformations. The average values of $\delta^{13}C$ in CB of the sedimentary cover are –29.5‰. Metamorphism and, especially, ore metasomatism, at the Sukhoi Log deposit caused a 2‰ increase in the heavy carbon isotope concentration of CB as compared to that of the platform deposits. The narrow variations in carbon isotope composition of the bitumoid are defined by their derivation from lipids, whose components are almost insusceptible to changes in the *PT* conditions. Kerogen from platform deposits is more strongly depleted than CB in the heavy carbon isotope ($\delta^{13}C_{av}$ –32.2‰). The insoluble carbonaceous matter (ICM) of the metamorphic shales is significantly enriched in the heavy carbon isotope ($\delta^{13}C_{av}$ –21.9‰). The highest changes in carbon isotope composition were found in concentrates of ICM from metasomatically altered rocks of the Sukhoi Log deposit ($\delta^{13}C_{av}$ –17.5‰). The heavier carbon isotope composition caused by metamorphism and metasomatism is evidently defined by isotopic exchange between the carbonate carbon and CO_2 of metasomatic solutions, on one hand, and ICM of shales, on the other.

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INTRODUCTION

Carbonaceous matter disseminated in sedimentary and metamorphic rocks is typically of organic origin. As it enters sediments and passes through all stages of lithification and metamorphism, the organic matter (OM) suffers destruction and carbon isotope fractionation. In Precambrian marine sedimentary rocks, carbonaceous matter has the lightest carbon isotopic composition (from –25 to –35 ‰). This is considered to be related to the specifics of the carbon cycle and biota composition in the ancient ocean [1–6]. The initial stages of transformation of the organic remains during sedimentation and diagenesis result in a change of the carbon isotopic composition toward variably negative values, depending on the setting in the sedimentation basin, owing to the destruction of OM components that were inherited from bioprecursors and have variable isotopic composition [7].

Carbon in ancient unmetamorphosed sedimentary rocks of different ages has low $\delta^{13}C$ values. In particular, throughout the Vendian–Devonian sedimentary sequence of the Russian platform cover, the carbonaceous matter (CM) is depleted in the heavy carbon isotope to $\delta^{13}C$ value of –30 ‰, with the bitumoid and kerogen having practically the same carbon isotopic composition [8].

The study of OM isotopic composition during catagenetic transformations (from proto- to mesocatagenesis) of caustobiolith indicates no significant changes in $\delta^{13}C$. An increase in $\delta^{13}C$ occurs in OM only during the final stage of apocatagenesis [9].

Wide variations in $\delta^{13}C$ were found in the ancient metamorphosed black shales and ore deposits in them. It was established that a temperature increase from 250 to 750°C during metamorphism is accompanied by isotope exchange between graphite and carbonate carbon, leading to an increase in $\delta^{13}C$ in graphite [10–13]. This made it possible to calibrate graphite–calcite geothermometer based on systematic fractionation of carbon isotopes with temperature: the temperature range of 200–700°C was calculated theoretically by Bottinga [11], and the range of 270–750°C was confirmed empirically by other researchers [10, 12, 13].

Complex interactions between organic and inorganic components of the rocks and influxes of CO_2-rich fluid during ore formation in carbonaceous sequences also likely leads to carbon isotope fractionation. In particular, deposits related to carbonaceous sequences demonstrate a zoned distribution of carbon and its stable isotopes. The Kumtor gold-bearing deposit in eastern Kirgyzstan demonstrates a compositional trend in the organic carbon content and a polymodal distribution of $\delta^{13}C$ varying from –19.4 to –32.9‰ [14]. The gold-bearing deposits of the Yenisei Range (Sovetskoe and Olympiadinskoe) have a zoned distribution of carbon isotopic ratios [15], which is related to the redistribution of components between organic matter and carbonates, carbon isotopic included, under elevated temperatures. A heavier carbon isotopic composition with $\delta^{13}C$ from –27.9 to –24.9‰ was found in the metasomatites and ores of the Muruntau gold-bearing field, western Uzbekistan, which are dominated by migrating (mobile) hydrocarbon species, unlike those in metamorphic rocks [16].

No systematized data are available on the carbon isotopic composition of the terrigenous–carbonate deposits of the Southern Siberian Platform and surrounding fold systems. This paper addresses the behavior of carbon isotopic composition in these sedimentary sequences during catagenesis, metamorphism, and metamorphic–metasomatic ore formation. This region contains the unique stratiform Sukhoi Log gold deposit, which is of great interest for geologists. Carbonaceous matter and its stable isotopic composition were further studied at the Sukhoi Log ores, in which carbon is a major component. Our newly obtained data on the carbon isotopic composition are interesting because of the scarcity of information on the carbon isotopic composition of the ores [17]. The aim of this work was to determine the dependence of the organic carbon isotopic composition on the metamorphic grade and local hydrothermal–metasomatic alterations.

CHARACTERISTICS OF THE SEDIMENTARY DEPOSITS

Sedimentary Cover of the Platform

The sedimentary cover of the southern Siberian platform consists of Precambrian (Riphean–Vendian) and Lower Paleozoic deposits 2.5–4 km thick (Fig. 1). These deposits are considered to be promising for oil–gas prospecting of this region [18]. The Upper Riphean supposedly includes carbonate deposits of the Olkha Formation, which occur over the Irkutsk area and were studied in the core of borehole 1. The Vendian deposits compose the Ushakov and Moty formations, and the Lower Cambrian deposits consists of the Usol'e, Bel'sk, Bulai, and Angara formations. These deposits are subdivided into two lithological–stratigraphic complexes: the terrigenous complex of the Vendian Ushakov Formation and the Lower Moty Subformation and halogen–carbonate sequence spanning the deposits of the Middle–Upper Moty subformations of the Vendian and the whole Lower Cambrian.

The Vendian platformal deposits were analyzed using core material on the Lower Moty Subformation from boreholes 159 (Dobchurskaya area), 15 (Korkinskaya area), and 139 (Preobrazhenskaya area). The deposits of the subformations are abundant in the southern part of the platform. These deposits consist mainly of sandstones, with subordinate gritstones, siltstones, and mudstones. The average C_{org} content (without carbonate carbon) in the sandstones varies from 0.30 to 0.60 wt %, occasionally reaching 0.85%.

The Lower Cambrian deposits (Bel'sk Formation) were studied in the core from borehole 12 at the Shamanovskaya area. The formation is composed of halogen–carbonate rocks from 150 to 320 m thick. The C_{org} is evenly distributed over the amphitheater area, accounting for from 0.14 to 0.20 wt %, at a maximum scatter of 0.01–0.30%. The rocks of the cover were subjected to several stages of mesocatagenesis (MC_{1-4}).

Surrounding Fold System

The Baikal fold area is the most abundant in the Neoproterozoic deposits, which accumulated mainly in the Baikal–Patom rift trough at the southern margin of the ancient Siberian craton (Fig. 1). The total thickness of these deposits varies from 5 km in the outer structural formational zones (Baikal and Lena areas) to 15 km in the inner (Bodaibo) zone. The sequence consists of alternating terrigenous and carbonate, often carbon-bearing rocks. The regional metamorphism is zonal. In the outer subplatformal zones, the metamorphic grades of these deposits range from metagenetic (apocatagenesis) to the sericite–chlorite subfacies of the greenschist facies. In the inner zone, metamorphism varies from the greenschist facies in the central part of the Bodaibo synclinorium to the amphibolite grade kyanite–sillimanite assemblage along its periphery [19]. The carbon isotopic composition was studied in the Upper Riphean black shales. Carbon-bearing silty pelites from the Dzhemkukan, Khomolkho, Aunakit, and Vacha formations in the Bodaibo synclinorium were collected in the borehole, and highly carbonaceous shales of the Kachergat formation in the western Baikal area were studied in exposures.

The Dzhemkukan Formation is located at the bottom of the Upper Riphean section. It consists of oligomictic and quartzose sandstones and siltstones alternating with chlorite–quartz–sericite, often carbon-bearnating metapelites, with a significant role of carbonaceous shales. Terrigenous rocks of the formation often contain carbonates. The C_{org} content in the shales varies from 0.10 to 3.90 wt %, averaging 1.12%.

The Khomolkho Formation is composed mainly of dark gray and black coal-bearing quartz–sericite–chlorite metapelites and siltstones, which contain up to 5–15 vol % sedimentary–diagenetic Mg–Fe ankerite–siderite carbonates. Quartz–feldspar, quartzose sandstones, and carbonate rocks occur in subordinate amounts. The sequence exhibits thin rhythmic bedding. The C_{org} content in the rocks varies from 0.05 to 7.0 wt %, averaging 1.5–2.0% in silty pelites. At the Sukhoi Log deposit, zones with ore metasomatic mineralization developed along the shale beds of the Khomolkho Formation. They are made up mainly of quartz, Fe–Mg carbonates, and pyrite with noble gold. At the same

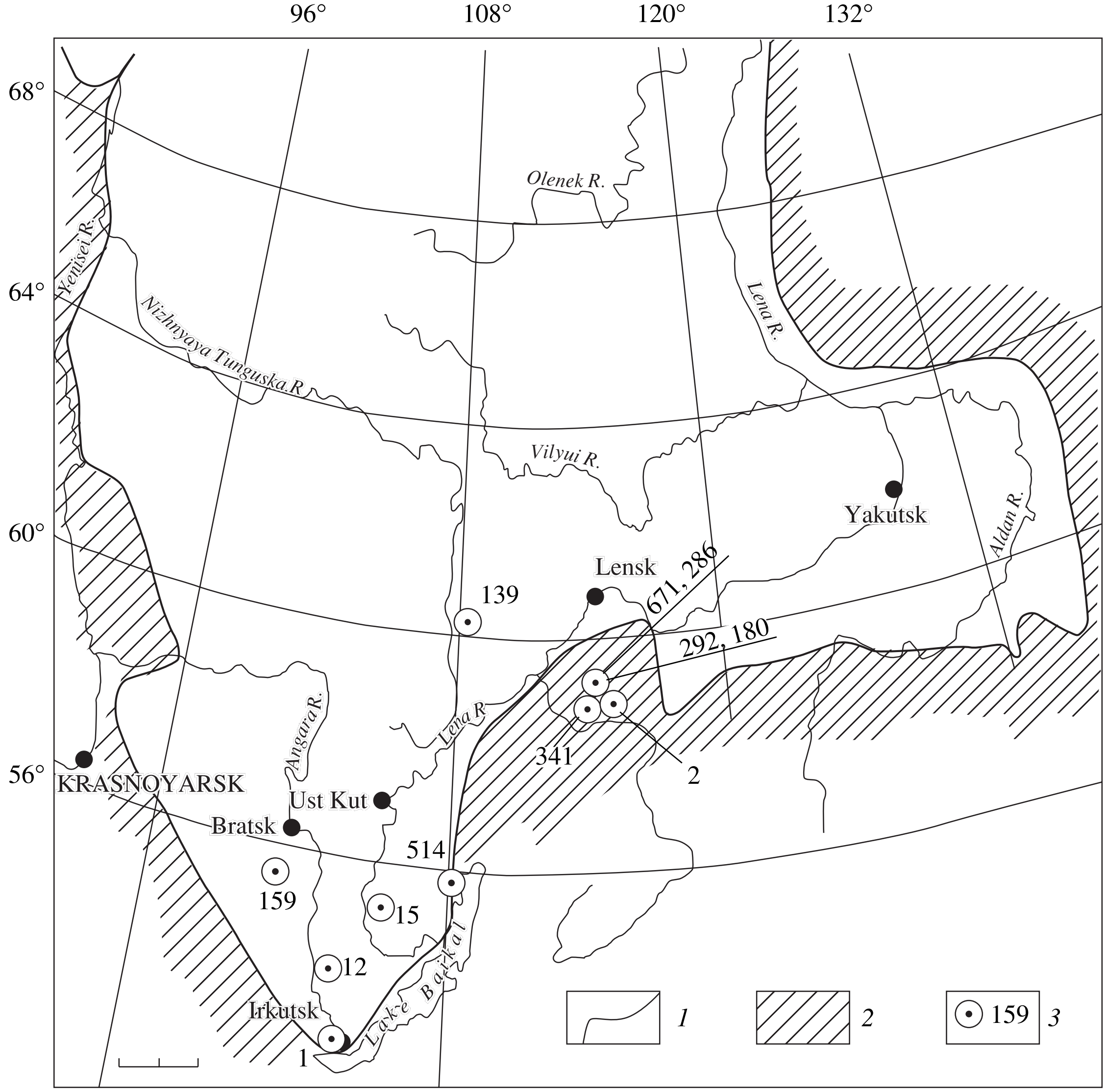

Fig. 1. Location scheme of the study areas. (*1*) Boundary of the Siberian Platform; (*2*) folded framing of the platform; (*3*) location and member of the borehole from which samples were taken.

time, exotic mineralization identified by electron–microscopic studies and consisting of PGEs and other native metals was formed during the metamorphic stage of ore formation under reduced conditions [20].

The Aunakit Formation consists of rhythmically alternating quartzose and oligomictic, often calcareous sandstones and calc–mica shales. The upper parts of the section are dominated by quartz–mica siltstones with C_{org} within 0.5–3.7 wt %, averaging 1.7%. The silstones contain sedimentary–diagenetic carbonates: up to 5–10 vol % siderite and up to 2–10 vol % ankerite.

The deposits of the Vacha Formation crown the Upper Riphean section in the Bodaibo synclinorium. The formation consists of carbonaceous quartzose sandstones, siltstones, and quartz–sericite shales and typically lacks carbonates. The sediments are thin bedded, often with traces of turbidity and submarine sliding, and have elevated C_{org} contents from 0.6 to 10 wt %, averaging 3.8% [21].

In western Transbaikalia, the Riphean is crowned by the Kachergat Formation of rhythmically alternating quartzose sandstones, sericite–quartz siltstones, and quartz–chlorite–sericite carbonaceous metapelites. Carbonates are absent. Upsection, the carbon content in the rocks increases to 20 wt %. The range of C_{org} content in the shales of the formation varies from 0.14 to 20.2 wt %, averaging 0.4–8.9 wt% at different levels.

METHODS

Scattered carbonaceous matter (SCM) of the terrigenous rocks from the southern Siberian platform and surrounding fold systems was studied in the whole-

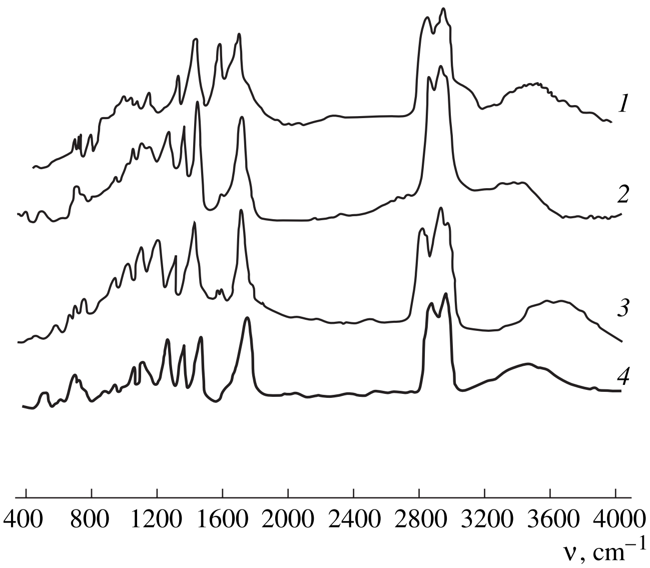

Fig. 2. IR spectra of chloroform bitumoids. (*1*) Sample 0658, sandstone of the Moty Formation; (*2*) sample 514-11, carbonaceous shale of the Kachergat Formation; (*3*) sample 341-96, carbon-bearing shale of the Aunakit Formation; (*4*) sample 292, carbon-bearing shale from the Sukhoi Log deposits.

rock samples, chloroform bitumoid (CB), and kerogen (insoluble carbonaceous matter (ICM)).

Shale samples were at first studied with thermal analysis on a Paulik–Paulik–Erdey derivatograph (MOM, Hungary). A kerogen thermogram (content of ICM) was obtained for each rock sample for comparison. The temperature at which carbonaceous matter started oxidizing (T_0°C) was correlated with the transformation grades of various carbonaceous rocks, which were arranged in order of increasing transformation grade (from catagenesis to metamorphism) [22].

The C_{org} content in the carbonate rocks and shales was determined via the standard method of sample combustion in a quartz pipe at 850–900°C in the presence of copper oxide [23]. Samples were preliminarily treated with 10% HCl (decarbonatization). Bitumoids were extracted by chloroform (CB) using cold extraction with subsequent separation of elemental sulfur using metallic Hg [24]. IR spectra of bitumoids were recorded on an UR-10 apparatus (film).

Cold extraction of insoluble carbonaceous matter (ICM) from debituminized rocks was performed by the techniques [25, 26]. The matter was repeatedly extracted from the rock by water flotation with petroleum ether. Combined residuum was dried, treated with HCl, and washed with H_2O. Then, the species was centrifuged to remove mineral impurities: carbonaceous matter was precipitated on a film for X-ray diffraction patterns that was preparatorily purified from emulsion.

Mass-spectrometric carbon isotopic analyses of initial rocks, bitumoids, and ICM (kerogen) concentrates were conducted at the Vernadsky Institute of Geochemistry and Analytical Chemistry by analysts L.I. Bannikova and M.P. Bogacheva. The measurements were made on a Varian MAT 230 mass spectrometer using the PDB standard. The measurement error was ±0.05‰, and the precision was no worse than ±0.3‰.

CARBON ISOTOPIC COMPOSITION OF DEPOSITS IN THE BAIKAL AREA

The epigenetic transformations of sediments in the platformal cover reach grades no higher than mesocatagenesis (MC), varying from its beginning of MC_1 to termination (MC_4), while rocks from surrounding fold systems were transformed from final stages of apocatagenesis (AC_3) to the epidote–amphibolite facies (Table 1). From catagenesis to metamorphism, ICM changes its mode of occurrence and structure. With increasing extent of transformations, carbonaceous matter improves its structure from X-ray amorphous species during the mesocatagenetic stage to disordered graphite in metamorphic schists. This is reflected in the systematic increase in the temperatures of the onset of oxidation reactions during thermal analysis of the ICM sample (Table 1).

Platformal Deposits

The carbon content (C_{org}) in the deposits of the southern Siberian platform varies within 0.21–0.85 wt %. The total range in the content of chloroform bitumoid in samples from the platformal cover is from 0.002 to 0.3 wt %. The highest contents of CB (hundredths and even tenths of a percent) were found in the rocks affected by early mesocatagenesis (MC_1–MC_2). In the Korkinskaya area, the rocks of the Moty Formation affected by MC_4 are depleted in bitumoid accounting for no more than a few thousandths of a percent.

IR spectroscopic data indicate that the *chloroform bitumoids* from platformal deposits have a similar composition. The presence of characteristic bands in samples CB is illustrated by the example of one sample (Fig. 2, *1*). IR spectrum shows the absorption bands of oxygen-bearing groups: acids, ketons, aldehydes, aromatic complex ethers (1710–1760 cm^{-1}), aromatic structures (1600 ± 30 cm^{-1}), unsaturated bonds of aliphatic structures and aromatic rings of different types of substitution (750, 820, and 880 cm^{-1}), methyl and methylene structures of paraffins (1390, 2950–2970 cm^{-1}), and hydroxyl and amynocompounds (3220–3450 cm^{-1}). According to these data, CB contains aliphatic, naphthene–aromatic hydrocarbons, and aliphatic and aromatic oxygen-bearing compounds.

Kerogen specimens from the studied deposits are highly dispersed brown matter. In some cases, nearly ash-free ICM concentrates were obtained (Table 2). The highly carbonaceous matter consists of carbon (91–94%),

Table 1. Carbon isotopic composition of sediments of different age from the southern Siberian Platform and surrounding fold system

Sample No., Borehole or exposures No., interval, formation, area	Degree of transformation	Rock/C_{org} (wt %)	T_0°C	CB (wt %)	$\delta^{13}C$ ‰		
					initial rock	CB	ICM
0658. borehole 159. 3546.8 m. Moty. Dobchurskaya	MC_1	Sandstone 0.6	240	0.22	–33.8	–29.1	–29.5
0659. borehole 159. 3406.0 m. Moty. Dobchurskaya	MC_1	Sandstone 0.7	300	0.015	–34.2	–30.6	–35.3
0626. borehole 139. 1726.0 m. Moty. Preobrazhenskaya	MC_1	Sandstone 0.85	300	0.30	–33.4	–29.0	–35.3
0577. borehole 12. 812.5 m. Bel'sk. Shamanovskaya	MC_1	Dolomite 0.21	320	0.013	–	–29.8	–30.5
1. borehole 1. 2051.5 m. Olkha. Irkutskaya	MC_2	Limestone 0.35	360	0.01	–28.2	–29.3	–27.6
0616. borehole 15. 2979-2987.0 m. Moty. Korkinskaya	MC_4	Mudstone 0.25	300	0.003	–30.7	–29.2	–31.5
0531. borehole 15. 2977-2978.5 m. Moty. Korkinskaya	MC_4	Sandstone 0.81	350	0.002	–32.0	–29.3	–32.6
514-11. exp.514. Kachergat. Pribaikal'skaya	AC_3	Shale 20.23	450	0.026	–34.3	–29.1	–35.8
341-96. borehole 341. 69-123 m. Aunakit. Bodaibinskaya	GR	Shale 1.71	600	0.0005	–21.09	–28.03	–21.60
341-209. borehole 341. 180-238 m. Aunakit. Bodaibinskaya	GR	Shale 3.09	600	0.0075	–21.1	–28.3	–21.1
341-352. borehole 341. 313-341 m. Aunakit. Bodaibinskaya.	GR	Shale 1.96	600	0.0015	–21.5	–28.9	–22.0
02. exp.2. Vacha. Bodaibinskaya	GR	Shale 4.11	590	0.0012	–	–28.5	–22.8
2-378. borehole 2. 114-642 m. Dzhemkukan. Bodaibinskaya	E-A	Shale 4.26	650	0.0005	–17.2	–28.9	–16.9
292. borehole 292. 88-93 m. Khomolkho. Sukhoi Log deposit	GR-MET	Shale 0.99	500	0.002	–17.9	–26.6	–17.6
180. borehole 180. 89-195 m. Khomolkho. Sukhoi Log deposit	GR-MET	Shale 0.7	620	0.003	–17.7	–27.7	–17.3
671. borehole 671. 63-65 m. Khomolkho. Sukhoi Log deposit	GR-MET	Shale 1.69	630	0.0025	–18.1	–27.5	–17.4
286. borehole 286. 91-105 m. Khomolkho. Sukhoi Log deposit	GR-MET	Shale 0.85	600	0.0031	–18.5	–27.0	–17.9

Note: $(MC)_{1-4}$ are stages of mesocatagenesis. (AC_3) apocatagenesis. (GR) and (E-A) are greenschist and epidote–amphibolite metamorphic facies. (GR-MET) green-schist facies overprinted by metasomatism. T_0 °C is the temperature of the beginning of exothermal peak at the thermogram of carbonaceous matter.

Table 2. Chemical composition of ash-free kerogen concentrates

Sample No.; area, formation, rock	Elemental composition, %			
	C	H	N	S
0626. Preobrazhenskaya, Moty, sandstone	86.06	6.26	1.10	1.90
0531. Korkinskaya, Moty, sandstone	91.44	3.44	n.d.	0.95
0659. Dobchurskaya, Moty, sandstone	91.14	5.67	0.91	1.17
292. Sukhoi Log, Khomolkho, carbonaceous shale	95.44	2.24	tr.	0.04

hydrogene (3.44–6.26%), sulfur (0.95–1.90%), and nitrogen (0.91–1.10%).

Bitumoids and kerogen from platformal deposits have similar isotopic compositions, as is exemplified by samples 0658 and 0577 (Table 1). Isotopic composition of chloroform bitumoids varies within a narrow range from –30.6 to –29.0‰, averaging –29.5‰. Kerogen from the same samples has a wider scatter of $\delta^{13}C$ from –35.3 to –27.6‰, at average values of –31.7‰.

Rocks from the surrounding fold systems

The least metamorphosed and most carbonaceous sediments among those studied in the surrounding rocks (Fig. 1) are shales of the Kachergat Formation in western Transbaikalia (C_{org} up to 20 wt %). They have a high content of CB (0.026 wt %). The IR spectrum of CB is similar to that of platformal deposits (Fig. 2, *2*), with less intense absorption bands of aromatic compounds. The carbon isotopic composition of ICM ($\delta^{13}C$ = 35.84‰) and bitumoid ($\delta^{13}C$ of 29.09‰) is similar to most data on platformal deposits. These rocks are located in the transition zone from catagenesis to metamorphism and were affected by the apocatagenetic stage (AC_3). The carbon isotopic composition of SCM remained unchanged.

The studied shales of the Aunakit and Vacha formations of the Baikal–Patom highland were metamorphosed under the greenschist facies. Having a bulk average carbon content of no more than 3.6 wt %, they have bitumoid concentrations as low as 0.001–0.0015% (Table 1).

The IR spectra of CB from the greenschist facies are similar and consist mainly of groups of complex ethers, acids, aldehydes, and hydrocarbon structures. Aromatic structures are absent (Fig. 2, *3*). CB in shales have similar isotopic composition, with $\delta^{13}C$ varying from –28.0 to –28.9‰ ($\delta^{13}C_{avCB}$ = –28.4‰). The carbon isotopic composition of CB from these formations is slightly (by no more than 1‰) enriched in $\delta^{13}C$ as compared to the CB of the platformal deposits.

Shales of the Vacha and Aunakit formations contain highly dispersed black ICM consisting of disordered graphite, as was identified by X-ray diffraction and thermal analysis. The whole-rock samples and ICM concentrates have similar carbon isotopic composition ($\delta^{13}C_{av}$ –21.2‰ and –21.9‰, respectively), which is caused by extremely low CB contents in the rocks. From catagenesis to metamorphism, the carbon isotopic composition of shales from the Aunakit and Vacha formations is shifted toward heavier carbon isotope values.

Carbonaceous shales of the Dzhemkukan Formation were metamorphosed under the epidote–amphibolite facies (Table 1). The bitumoid content in the rocks decreases to 0.0005%. IR spectroscopic data indicate that the CB in shales of this formation is compositionally similar to the CB from lower grade shales. The values of $\delta^{13}C$ in bitumoids (–28.3‰) also correspond to those in CB from shales of the Aunakit and Vacha shales. A much heavier carbon isotopic composition was found in the ICM from this shale ($\delta^{13}C$ = –16.9 ‰). Thus, the carbon isotopic composition of ICM became heavier by 5‰ from greenschist to epidote–amphibolite facies (Table 1).

The carbonaceous shales from the Khomolkho Formation of the Sukhoi Log deposit contain from 0.7 to 1.69 wt % organic carbon and 0.002-0.0031% bitumoids (Table 1). The IR spectra of CB is similar to those of bitumoids from the Aunakit and Vacha shales. They also consist mainly of bands of carbonic acids, aldehyde, ketons, paraffins, and methane–naphthene hydrocarbons (Fig. 2, *4*).

The carbon isotopic composition of CB varies from $\delta^{13}C$ = –27.8 to –26.6‰ at $\delta^{13}C_{av}$ of –27.20‰. Thus, the carbon isotopic composition of CB in shales from ore zones varies insignificantly as compared to that from the Aunakit and Vacha formations ($\delta^{13}C$ of 28.3‰), showing no more than 1‰ enrichment in the heavy carbon isotope relative to the less altered rocks.

ICM samples consist of highly dispersed black matter, whose ash-free concentrates with 95.44% carbon contain about 2.24% H and an insignificant content of heteroelements (Table 2). This highly carbonaceous matter is disordered graphite, as in the ICM concentrates from barren beds [27].

The $\delta^{13}C$ values in shales from the Khomolkhin Formation in the mineralized intervals of the Sukhoi Log deposit ($\delta^{13}C_{av}$ of 18.0‰) and ICM concentrates ($\delta^{13}C_{av}$ of 17.5‰) from the same rocks showed that the formation of the ore was accompanied by significant fractionation of carbon isotopes, associated with the enrichment of ore zones in heavy isotopes relative to the host rocks outside the ore field (Aunakit and Vacha formations), though both shales were metamorphosed to the greenschist facies.

DISCUSSION

As follows from literature data [1–8], organic matter that precipitated in ancient marine sedimentation basins is significantly depleted in ^{13}C. According to recent concepts, this is related to the mechanism of photosynthesis in ancient algae and/or CO_2 variations in the early Earth atmosphere, both mechanisms favorable for stronger isotope fractionation [7, 8]. The stability of lipid components of OM under a broad range of lithification and diagenesis conditions facilitated the preservation of the isotopic signatures of bioprecursors in sediments. The polymerization of OM during diagenesis could lead to the further lightening of the carbon isotope composition [7]. Hence, the features noted in the isotopic composition of carbonaceous matter in the studied deposits, including similar composition of bitumoids and kerogen, are well consistent with the sapropel type of initial OM in sediments and confirms its biogenic origin. The heavy isotopic composition of carbonates in the carbonaceous deposits might significantly affect carbon isotope exchange in the sedimentary sequences during subsequent metamorphic transformations [10].

The data presented above (Table 1, Fig. 3) indicate that the carbonaceous matters in the catagenetically altered deposits of the Siberian platform cover have the following features: (1) kerogen is significantly enriched in the light carbon isotope (δ^{13}C from –27.6 to –35.8‰); (2) kerogen and bitumoid have a similar carbon isotopic composition; (3) bitumoid has almost unvarying δ^{13}C values, which are, on average, 2‰ higher than those of kerogen. This implies that the dissolved components of SCM have stable isotopic ($\delta^{13}C_{av}$ = –29.4‰) and chemical compositions (IRS) during catagenesis, regardless of the composition of pristine rocks. The variations in the δ^{13}C in kerogen within 8‰ during the catagenetic stage were likely controlled by the variable extent of transformation of OM components in the initial sediment.

Highly carbonaceous shales of the Kachergat Formation, which experienced apocatagenesis and are confined to the transition zone from platformal (mesocatagenesis) to metasedimentary deposits of the fold system, show no significant differences from the sedimentary cover of the Siberian platform in terms of carbon isotope composition of bitumoids and kerogen (Table 1). This indicates that the apocatagenetic transformation of sedimentary rocks also does not exert any significant effect on the carbon isotopic composition of the shales.

It should be noted again that bitumoids in the catagenetically altered deposits have a more stable carbon isotopic composition than kerogen, which shows wider variations in δ^{13}C compared to the soluble fraction of OM.

In the metamorphosed rocks of the fold system, the carbon isotope distribution in the SCM of shales sharply changes. The carbon isotopic composition in the pristine rocks and ICM from the carbonaceous shales of the Aunakit and Vacha formations metamorphosed to the greenschist facies significantly differ from those in the platformal cover (Table 1). The soluble fraction of SCM preserves a little varying carbon isotopic composition ($\delta^{13}C_{av}$ = –28.2‰)), enriching in δ^{13}C by no more than 1 ‰ as compared to the carbon isotopic composition of CB from platformal rocks that experienced only catagenesis.

The CB of green schists contain aliphatic, methane–naphthene hydrocarbons, and complex ethers of carbonic acids but no aromatic compounds, a fact indicating further destruction of OM [19]. At the same time, the carbon isotopic composition of shales and ICM concentrates from the Aunakit and Vacha formations becomes significantly richer in the heavy carbon isotope: $\delta^{13}C_{av}$ = –21.2‰ and –21.9‰, respectively.

The carbon isotopic composition in the bitumoids from the epidote–amphibolite facies shales of the Dzhemkukan Formation is similar to that in low-temperature shales (Table 1). However, ICM in them shows strong enrichment in δ^{13}C (δ^{13}C = –16.9‰). The decomposition of siderite–ankerite carbonates at greenschist to epidote–amphibolite facies conditions could cause the enrichment of graphite in the heavy carbon isotope. Hence, the isotopic effects observed in the ICM of the shales with δ^{13}C enrichment were controlled by the metamorphic conditions, in particular, the high temperature, which causes isotopic exchange between carbon of carbonates and organic components of the rock.

The amount of bitumoids in the shales decreases by one to two orders of magnitude with increasing metamorphic grade, which is caused by the destruction of organic matter with increasing temperature. This indicates that the bitumoids are the initial OM of the sediments and are syngenetic to kerogen, which was formed during their decomposition. Small amounts of bitumoids contained in the closed pores of the rocks appeared to be isolated from reactions proceeding in the rock and retained their isotopic composition, which is close to that of the initial OM of the marine sediments (Fig. 3).

At the Sukhoi Log deposits, the Khomolkho shales of the albite–ankerite–sericite metamorphic zone were overprinted by ore-related metasomatism. In spite of the low-grade metamorphism, the carbon isotopic composition of ICM reached the same values as in the shales of the epidote–amphibolite facies ($\delta^{13}C_{av}$ = –17.6‰), which is related to metasomatic alterations. The decarbonatization of the prevading diagenetic Fe–Mg carbonates (ankerite, siderite) accounting for 5–15 vol % of the rocks, could enrich hydrothermal

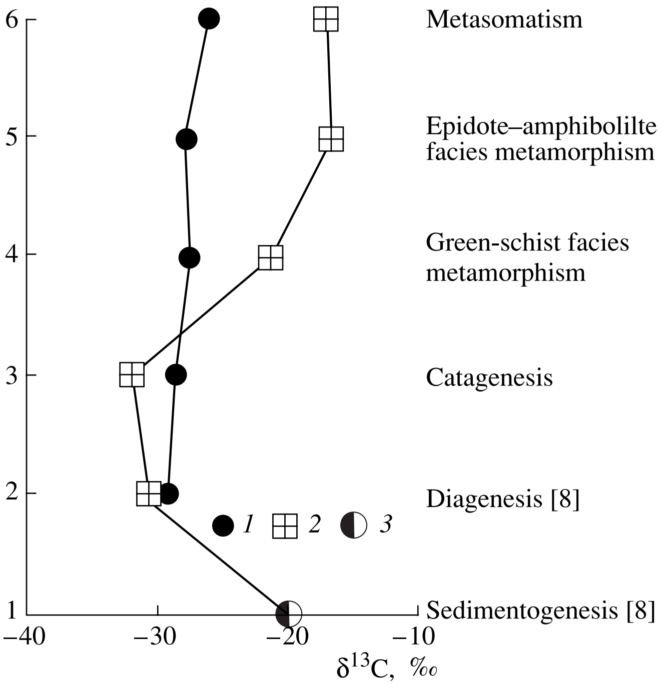

Fig. 3. Variations in the carbon isotopic composition of sedimentary rocks versus the degree of postsedimentation transformations of carbon-bearing deposits: (*1*) chloroform bitumen, (*2*) insoluble carbonaceous matter (kerogen); (*3*) planktonic matter [8].

solutions in CO_2 with an elevated ^{13}C content. Data on gas–liquid inclusions in quartz from the Sukhoi Log deposit confirmed the high contents of carbonic acid in residual solutions [27]. The recrystallization of ICM in such an environment caused a heavier carbon isotopic composition.

The Sukhoi Log deposit was formed in a carbonaceous environment initially enriched in noble and nonferrous metals [21, 28]. During ore formation, ICM could be aggregated with the metals. It was found out that microscopic-sized particles of native metals, in particular, Pt [29], are mainly coated with insoluble carbon, indicating that the metal was not introduced but precipitated *in situ* during the initial metamorphic stage of ore formation under greenschist facies conditions (420–380°C, 5–6 kbar [19, 20]), from metalliferous naphthide component of carbonaceous matters. Under such conditions, at oxygen shortage, the metals were reduced to native state and often coated by carbon film. This is accompanied by the removal of isotopically light gaseous carbon compounds (for example, methane) and the enriching of the remaining carbon in ^{13}C. In this context, the fact that carbonaceous matter, a major component of the black shales, participates in the ore-forming processes is confirmed, to a certain degree, by the data on carbon isotope fractionation.

In general, the distribution of carbon isotopes between SCM components suggests a significant (drastic) ^{13}C enrichment of kerogen (ICM) from catagenetic to metamorphic stages and a gentle growth of $\delta^{13}C$ in the bitumoids (CB) with increasing metamorphic and metasomatic grade (Fig. 3).

CONCLUSIONS

The light carbon isotopic composition of sedimentary deposits at the Siberian platform, which were the least altered by younger processes, was inherited from phytoplankton, their bioprecursor. During the diagenesis of the sediments, OM enriches in the lighter carbon isotope because of the relatively higher stability of lipids. The diagenesis of carbonaceous sediments is accompanied by the formation of authigenic carbonates, having the heavier carbon isotopic composition.

Catagenesis (from proto- to apocatagenesis) does not significantly affect carbon isotope fractionation, presumably indicating that carbon did not participate in exchange and redox reactions during this stage.

Under prograde metamorphism and subsequent metasomatism, the carbon of ICM becomes isotopically heavier owing to isotopic exchange with the carbon of carbonates or the CO_2 of hydrothermal solutions. Also, an increase in temperature and pressure under reduced conditions leads to the reduction of OM of the rocks with the removal of isotopically light gaseous hydrocarbons: CH_4 and others. Our results show that the initially isotopically light organic carbon of sedimentary rocks could be fractionated only at high *PT* parameters in the presence of carbonate mineralization or CO_2-rich solutions, i.e., during metamorphism and metasomatism. In this case, the carbon isotopic composition of bitumoid, a soluble OM fraction, whose small amounts were preserved in closed pores, retains the isotopic composition of the bioprecursor.

Chloroform bitumoids show stable $\delta^{13}C$ values within a wide range of postsedimentation transformations. Metamorphism and metasomatism only weakly shift the carbon isotopic composition of the CB of shales and rocks in the ore zones toward heavier values relative to those of the sedimentary cover.

The carbon isotopic composition of ICM (kerogen) might indicate a degree of transformation of the primary sapropel-type sediments during catagenesis, metamorphism, and ore formation in the sedimentary deposits of the southern Siberian platform and its surrounding fold systems.

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