

Isotopic Evidence for Postsedimentary Transformation of Rocks of the Lower Cambrian Angara Formation in the Irkutsk Amphitheater

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Abstract—The section of the Angara Formation (upper portion of Lower Cambrian) is composed of a complex combination of dolomites, anhydrites, marlstones, and salinastones. The occurrence of solution breccia, various types of metasomatism, and other indications testify to the substantial postsedimentary reworking of these rocks. Sulfate reduction, one of the most important processes of reworking, is clearly expressed in the sulfur isotopic composition. The ⁸⁷Sr/⁸⁶Sr ratio in carbonate and sulfate materials is more stable owing to the relatively high Sr content in these rocks. Nevertheless, most sulfate and carbonate rocks are contaminated with the radiogenic Sr. The carbon isotope ratio in carbonates is close to the “normal” value despite the evaporitic character of sedimentation basins and the possible participation of organic carbon, which is a product of the oxidation of hydrocarbons by sulfates, in the transformation of carbonates. The Rb–Sr analysis of the clayey component of marlstones and the K–Ar analysis of mudstones from the lower portion of the Lower Cambrian–Vendian section indicate that the rocks were mainly transformed during a time span corresponding to the Caledonian folding dramatically manifested at the platform margin.

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INTRODUCTION

The isotopic study of Neoproterozoic and transitional Neoproterozoic/Paleozoic rocks are widely used for the reconstruction of sedimentation paleoenvironment and chemostratigraphic correlations (Jacobsen and Kaufman, 1999; Veizer et al., 1999; Walter et al., 2000; Goldberg et al., 2005; Halverson et al., 2005, 2006; Melezhik et al., 2005). This interval of geologic history attracts special interest due to two reasons. Precisely this time was marked by the widest variations in the isotope ratio, and the possibility of biostratigraphic correlation becomes very limited (or disappears) since the Early Cambrian. The traditional use of isotopic methods for these purposes is based on the assumption of geochemical invariability of rocks and retention of their isotopic systems since the early diagenesis. In some cases, the suggestion of geochemical invariability of rocks is supported by lithological and geochemical investigations. In other cases, this is taken merely on trust. At the same time, results of many investigations suggest that rock compositions are constantly transformed (Vinogradov, 2003; Cai et al., 2003; Uysal and Golding, 2003; Kholodov, 2004; Desrocher et al., 2004; Adams et al., 2005; Yapaskurt, 2005; Rasmussen, 2005;

and others). During the entire period of existence, rocks interact with saturating or circulating solutions, resulting in mineral, isotopic, and other compositional transformations. We designate these transformations by the general term “epigenetic,” which is equivalent to “postsedimentary.” The rate of such commonly not great transformation markedly increases at particular moments of geologic history. However, the rate depends on rock composition in all cases. The alteration is maximum in sulfate–salinastone (anhydrite–halite) rocks. However, precisely these rocks seem to be most conservative (with respect to shifts of the isotopic composition) because of high contents of the studied chemical elements.

The Neoproterozoic/Early Paleozoic boundary is marked by one of the most significant maximums of salt deposition. A great number of direct and indirect evidences in favor of salt occurrences in the older Neoproterozoic sequences are also known. Precisely these circumstances compelled us to turn to the East Siberian Vendian–Cambrian saliferous basin in order to estimate the degree and, if it is possible, the timing of variations of initial isotope ratios in the enclosing rocks. This issue is important not only for the estimation of geochemical implications of epigenetic pro-

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cesses, but also for the isotopic-stratigraphic correlation.

Results of the first cycle of works devoted to the lowermost portion of the Vendian–Cambrian sequence are reported in (Vinogradov et al., 2006a–2006c). In the present paper, we report new data on the ongoing investigation of rocks of the Angara Formation (the uppermost Lower Cambrian). It is noteworthy that rocks from various parts of the sequence are characterized by appreciably different degrees of secondary alteration. The choice of the Irkutsk Amphitheater was dictated by the availability of excellent monographic lithological descriptions of rocks from this district (Pisarchik, 1963; Pisarchik and Minaeva, 1975) and the preservation of cores from some boreholes. The studied samples were taken from Pisarchik's collections.

SPECIFIC FEATURES OF THE STRUCTURE OF STUDIED SECTIONS

The general stratigraphic scheme of Cambrian sequences in the Irkutsk Amphitheater (*Resheniya...*, 1989) is reproduced in Table 1.¹ Previously, we described the Lower Cambrian section based on boreholes drilled in the Bel'sk and Zhigalovo areas (Vinogradov et al., 2006a). We sampled the section of the Angara Formation in boreholes 54 and 33 drilled near the Settlement of Markovo approximately 350 km north of Borehole Zhigalovo. Lithology of rocks is described in (Pisarchik, 1963). In general, rocks of the Angara Formation in the Irkutsk Amphitheater are distinguished by extremely spectacular and distinct manifestations of the secondary alteration that attracted our attention. The sections can be divided into the sulfate–carbonate and sulfate-free types.

The sulfate–carbonate sequences are devoid of calcitization in compliance with the absence of primary limestones in such sections noted in (Pisarchik, 1963, p. 144). In the studied sulfate-free sequences, the secondary desulfatization is widespread. Sulfate reduction and desalinization led to a systematic decrease in the total thickness of rocks. Dolomite and anhydrite are often replaced with the secondary calcite. Consequently, the rocks represent a complex chloride–sulfate–carbonate mixture. In the sulfate–carbonate sequences, these processes are poorly expressed. In the sulfate-free sequences, the pure anhydrite interbeds are virtually absent. However, we also failed to find the sulfate-free samples. The sulfate content in rocks from such sequences commonly ranges from n to $10n\%$. These sequences are characterized by the abundance of secondary breccias formed after chloride or sulfate

Table 1. Stratigraphic scheme of the Vendian–Cambrian sequence in the Irkutsk Amphitheater

System, series	Formation, thickness, m	Lithology	
Є ₃	Verkhnyaya Lena, 450–800	Sandstone, siltstone, and dolomitic marlstone with anhydrite at the base	
	Є ₂	Litvintsevo, 100–150	Dolomite and solution breccia
Є ₁		Angara, 380–600	Dolomite, rock salt, and anhydrite
	Bulai, 120–145	Dolomite	
	Bel'sk, 300–450	Rock salt (at top), dolomite, and anhydrite	
	Usol'e, 600–1000	Rock salt, dolomite, and anhydrite	
V	Moty	upper	Dolomite, marlstone, and anhydrite
		middle	Dolomite, sandstone, anhydrite, and marlstone
		lower	Quartz sandstone
	Ushakovka, 100–500	Sandstone, siltstone, and anhydrite	

rocks. Boreholes drilled in this region often cross fault zones with inclined (occasionally, very steep) rocks related to the hydration of anhydrites and salt diapirism. Mineral and compositional transformations of rocks are indicated by the abundance of indications of dolomite solution; the development of caverns in carbonate rocks, their stylolitization, and secondary silicification; the presence of newly formed celestine, fluorite, barite, and native sulfur; the distinct smell of hydrogen sulfide (during the crushing of samples, in particular); and other lithostructural changes. Data on the wide development of sulfide waters (including waters with a very high concentration of hydrogen sulfide) in the Angara–Lena Basin are presented in (Pinneker, 1966; Plotnikova, 1977). The almost complete absence of primary silicate rocks in the Angara Formation is noteworthy. These rocks occur as an insignificant component at the base and roof of the Angara Formation and in insoluble fractions of the clayey varieties of dolomite and anhydrite.

Figure 1 shows schematic lithological columns of the two sampled boreholes.

EXPERIMENTAL

The sampling system was predetermined by the availability of cores and the striving for maximal characterization of the Angara section.

¹ In previous publications, we used the stratigraphic scheme proposed by Pisarchik (1963). New schemes proposed for various regions of the Siberian Platform use special nomenclatures that cannot always be correlated with sections of the Irkutsk Amphitheater. Therefore, we retained previous stratigraphic names in the present paper. However, the Ushakovka and Moty formations are referred to the Vendian in accordance with modern concepts.

Angara Formation

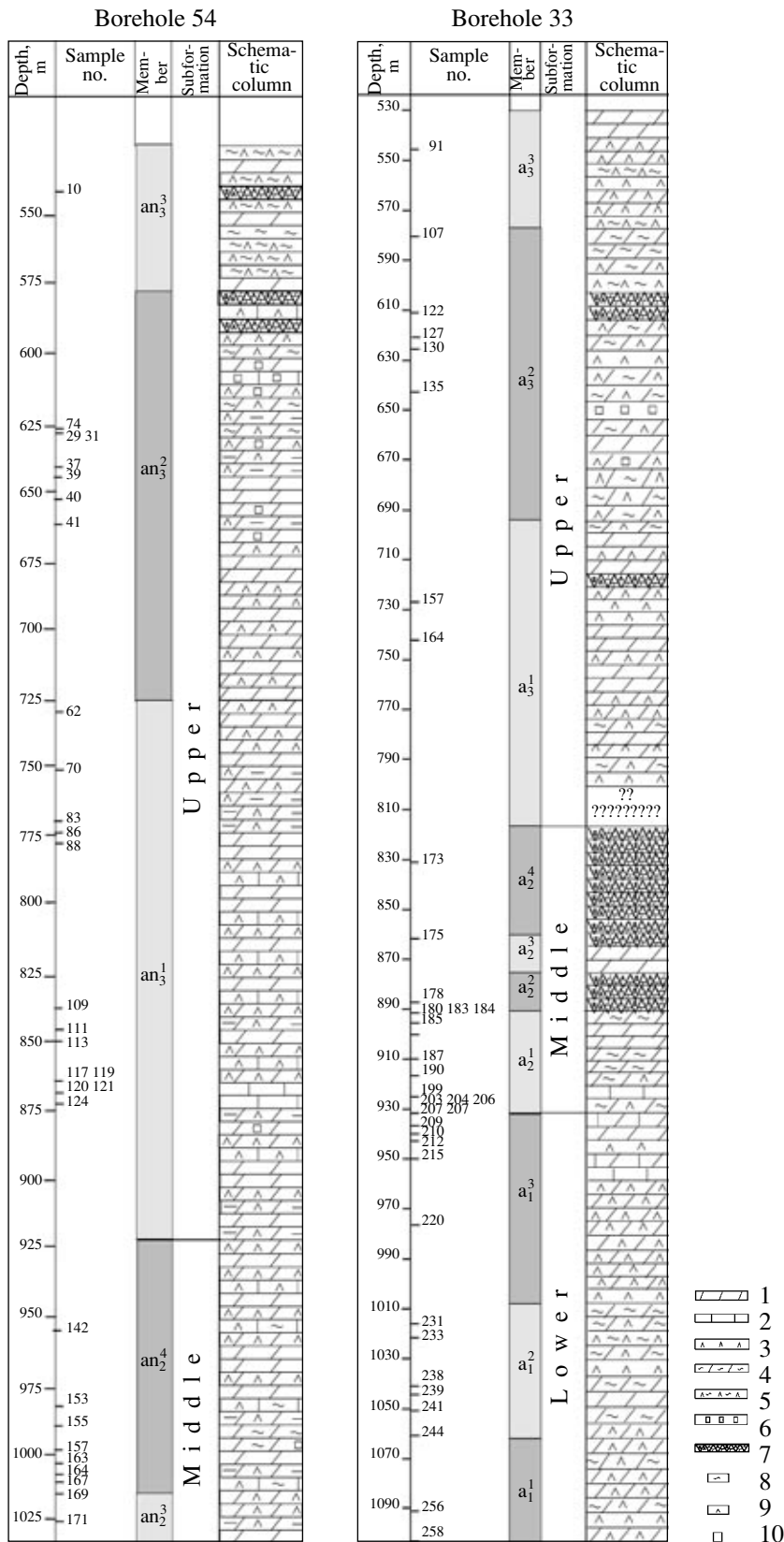


Fig. 1. Schematic lithological columns of the Angara Formation and sample location in the section. (1) Dolomite, (2) limestone, (3) anhydrite-gypsum, (4) clayey dolomite and dolomitic marlstone, (5) clayey anhydrite, (6) rock salt, (7) solution breccia, (8) admixture of clayey material, (9) admixture of sulfate material, (10) salt impregnation.

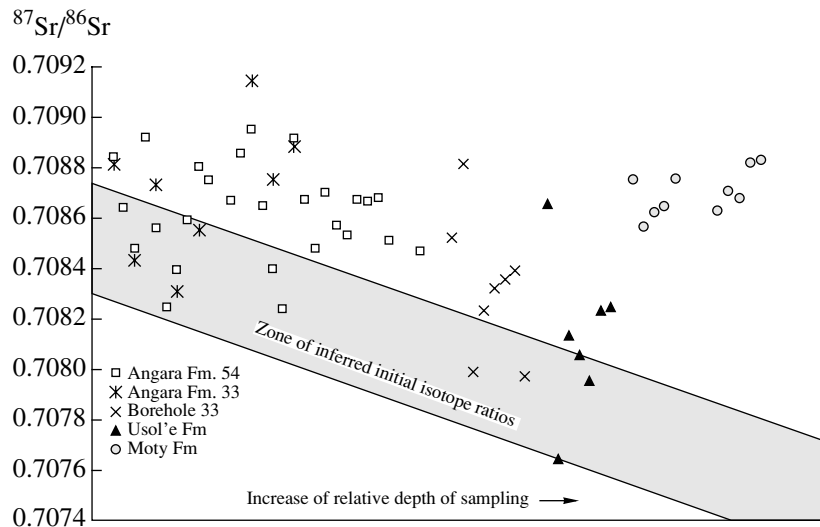


Fig. 2. $^{87}\text{Sr}/^{86}\text{Sr}$ values in carbonates and sulfates from Vendian–Cambrian rocks of the Irkutsk Amphitheater.

All measurements were carried out in the Isotopic Laboratory of the Geological Institute, Russian Academy of Sciences. The preparatory and measuring procedures have been described in our previous publications (Vinogradov et al., 2006a–2006c). Some specific features of sample processing were related to their chemical inhomogeneity. In order to study the Rb–Sr system, we separated the sulfate, carbonate, and silicate components of marlstones. First, we dissolved the sulfate fraction of samples in water on the vibration table. This procedure took several weeks in some cases. After checking the completion of the process by a qualitative reaction for BaSO_4 , the residue was treated with 2 N HCl to dissolve the carbonate fraction. The duration of acid treatment varied from a few minutes to a few hours. The insoluble residue (IR) was washed out and used for Rb–Sr measurements. Since standardization of such a procedure is difficult, we obtained different results in replicate runs with the same samples, particularly, in the case of Rb–Sr measurements in the insoluble residue and carbonate fraction.

Uncertainty of measurements of the Rb/Sr ratio estimated from replicate measurements of the ISG-1 standard (Vinogradov and Chernyshev, 1987) was not worse than $\pm 1\%$. Measurement error of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was ± 0.0002 .

RESULTS AND DISCUSSION

Strontium. Results of the Rb–Sr measurement in samples from the Angara Formation are given in Table 2, while the levels of sampling are shown under the respective numbers in Fig. 1.

Values of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in carbonates and sulfates, the main carriers of Sr in rocks, in the Lower Cambrian section are summarized in Fig. 2. Only samples with the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio not lower than 0.03 were

analyzed. In this case, variation in the Sr isotope ratio over ~ 500 Ma does not exceed the real uncertainty of $^{87}\text{Sr}/^{86}\text{Sr}$ measurements (0.0002). The zone of probable initial Sr isotope ratios shown in Fig. 2 embraces the interval of isotopic composition variation in the Vendian–Cambrian seawater. The complex character of this variation is seen from the plot (Fig. 3) based on the gen-

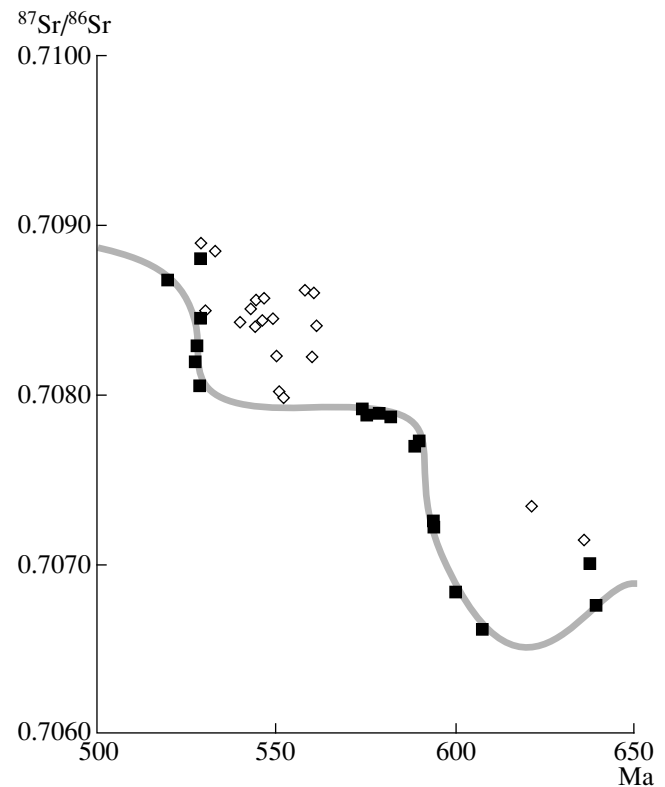


Fig. 3. Sr isotopic composition in the Late Neoproterozoic–Cambrian seawater. Filled symbols designate the least altered samples (Walter et al., 2000).

Table 2. Results of Rb-Sr measurements (Angara Formation, boreholes 54 and 33)

Sample no.	Analyzed material	Depth, m	$\frac{^{87}\text{Sr}}{^{86}\text{Sr}}$	$\frac{^{87}\text{Rb}}{^{86}\text{Sr}}$	Sr, ppm	Rb, ppm
Borehole 54						
10	Brecciated anhydrite–gypsum	541	0.70935	0.0003	1950	0.18
29	Clayey gypsum–anhydrite, IR	627	0.73914	4.758	8.80	14.41
29	Sulfate	627	0.70884	–	–	–
31	Dolomite–anhydrite, sulfate	628	0.70864	–	–	–
37	Carbonate	635	0.70850	0.024	31.7	0.26
39	Anhydritic–dolomitic marlstone, IR 1	641	0.76720	8.00	2.83	7.68
39	Anhydritic–dolomitic marlstone, IR 2	641	0.78820	10.10	1.50	4.99
39	Sulfate	641	0.70892	0.001	1380	0.16
39	Sulfate	641	0.70856	0.0002	1380	0.113
39	Carbonate	641	0.70827	0.026	43.41	0.39
40	Ooidal–oolitic dolomite	656	0.70841	0.0176	59.03	0.34
41	Anhydritic–dolomitic marlstone, IR	660	0.78311	8.99	3.59	11.10
41	Carbonate	660	0.70882	0.020	49.48	0.337
74	Dolomitic–anhydritic marlstone, IR	657	0.81778	16.05	0.686	3.68
62	Intercalated anhydrite and dolomite, sulfate	731	0.70859	0.0001	1230	0.044
70	Dolomitic marlstone, IR	753	0.86292	21.93	3.391	25.08
70	Carbonate	753	0.70884	0.0417	51.88	0.797
83	Dolomitic marlstone, IR	769	0.71735	1.241	129.6	55.5
86	Anhydritic–dolomitic marlstone, IR	775	0.71467	1.024	127.5	45.09
86	Anhydritic–dolomitic marlstone, IR	775	0.71290	0.687	215.5	51.15
86	Sulfate	775	0.70867	–	–	–
86	Carbonate	775	0.70875	0.083	80.39	2.30
86	Carbonate	775	0.70933	0.109	86.82	3.28
88	Carbonate	779	0.70886	0.006	239	0.48
109	Sulfate	839	0.70895	–	–	–
111	Anhydritic–dolomitic marlstone, IR 1	846	0.73650	4.44	13.84	21.2
111	Anhydritic–dolomitic marlstone, IR 2	846	0.71235	0.499	41.88	7.22
111	Sulfate	846	0.70866	0.015	1509	8.08
111	Sulfate	846	0.70840	0.001	1438	0.50
111	Carbonate	846	0.70893	0.016	45.93	0.25
113	Sulfate	851	0.70867	0.0004	1510	0.22
117	Dolomitic limestone, carbonate	865	0.70870	0.021	37.4	0.27
119	Dolomitic limestone, carbonate	867	0.70857	–	–	–
120	Dolomitic limestone, carbonate	871	0.70857	0.04	329	4.6
121	Dolomitic limestone, carbonate	871	0.70869	0.021	257.4	1.9
124	Anhydritic–dolomitic marlstone, IR 1	876	0.80110	16.11	4.71	25.95
124	Anhydritic–dolomitic marlstone, IR 2	876	0.76720	10.26	6.77	23.8
124	Sulfate	876	0.70872	0.06	1024	22.5
124	Sulfate	876	0.70868	0.001	1608	0.58
124	Carbonate	876	0.70853	0.022	61.6	0.46
142	Sulfate	954	0.70848	–	–	–
153	Carbonate	985	0.70950	0.019	147.3	0.946
153	Carbonate	985	0.71229	0.346	55.56	6.65

Table 2. (Contd.)

Sample no.	Analyzed material	Depth, m	$\frac{^{87}\text{Sr}}{^{86}\text{Sr}}$	$\frac{^{87}\text{Rb}}{^{86}\text{Sr}}$	Sr, ppm	Rb, ppm
155	Dolomitic marlstone, IR	987	0.81928	18.17	7.295	44.78
157	Clayey dolomite, IR	993	0.77475	9.17	17.83	55.97
163	Dolomitic marlstone, IR	1006	0.87919	25.12	9.83	83.1
163	Carbonate	1006	0.70865	0.133	44.49	2.038
164	Sulfate	1011	0.70909	–	–	–
164	Carbonate	1011	0.70872	0.155	116.4	6.24
167	Clayey anhydrite–dolomite, IR	1016	0.83147	16.03	11.68	63.9
167	Carbonate	1016	0.71125	0.278	124.5	11.97
169	Clayey anhydrite–dolomite, IR 1	1018	0.77403	8.056	12.42	34.4
169	Clayey anhydrite–dolomite, IR 2	1018	0.88784	22.96	10.59	82.6
169	Sulfate	1018	0.70868	–	–	–
169	Carbonate	1018	0.70943	0.0641	115.3	2.55
171	Clayey anhydrite–dolomite, IR	1027	0.79336	10.80	16.1	59.26
171	Anhydrite	1027	0.70847	–	–	–
Borehole 33						
107	Dolomitic marlstone, IR	580	0.78444	10.26	20.96	73.76
127	Dolomitic marlstone, IR	624	0.73145	3.19	11.00	12.09
141	Dolomitic marlstone, IR	652	0.72147	1.70	3.65	2.14
157	Anhydrite	728	0.70888	0.005	154.3	0.245
175	Solution breccia, carbonate	862	0.70875	0.017	28.58	0.17
184	Clayey dolomite, carbonate	895	0.71042	0.020	39.52	0.28
185	Dolomitic marlstone, IR	896	0.71366	0.67	72.3	16.7
187	Dolomite with stylolitic sutures	901	0.70881	0.009	27.1	0.086
190	Dolomitic marlstone, carbonate	910	0.74225	4.49	41.9	64.76
204	Saline dolomite	932	0.70843	0.0021	65.41	0.041
208	Dolomite with stylolitic sutures	935	0.70855	0.0015	775.2	0.40
210	Dolomitic limestone, carbonate	940	0.70838	–	–	–
220	Dolomite–anhydrite, carbonate	975	0.70914	0.022	30.15	0.23
231	Dolomitic marlstone, IR	1016	0.71123	0.45	55.40	8.57
233	Dolomitic marlstone, IR	1027	0.75030	5.89	15.74	31.93
238	Dolomitic marlstone, IR	1041	0.80352	13.08	16.35	73.2
239	Dolomite	1044	0.70873	0.037	74.26	0.95

Note: (IR) Insoluble residue; (–) no data.

eralization of data from different provinces of the world (Walter et al., 2000).

Even taking into account a large uncertainty in the estimation of initial Sr isotope ratios, most samples are contaminated with radiogenic Sr (Fig. 2). This is especially evident for rocks of the Moty Formation. The lower portion of this formation and the underlying Ushakovka Formation are composed of terrigenous rocks. Rocks of the Angara Formation are contaminated to a lesser extent. Sr isotope ratio in these rocks is often

close to the inferred initial values, probably, owing to the almost complete absence of terrigenous rocks and the insignificant admixture of the silicate component in marlstones.

Several geochemical criteria allow us to judge the possible retention (or, alteration) of the initial Sr isotope ratio in carbonates. However, none of them may be admitted as an absolute criterion. The Sr content in a sample is regarded as the most reliable indicator, because it is more difficult to shift the initial isotope

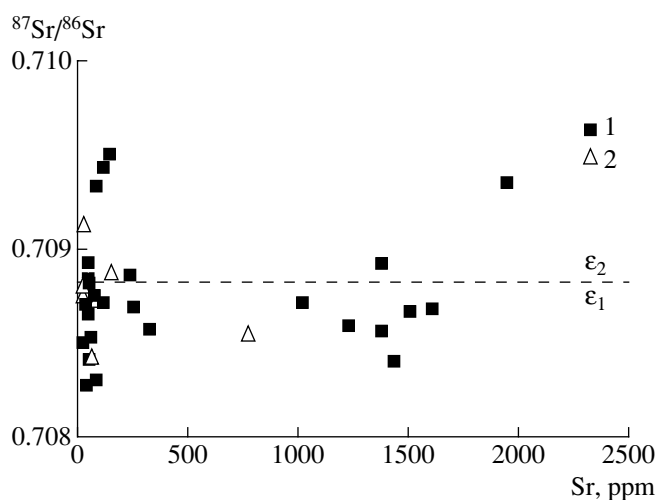


Fig. 4. $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Sr relationship in sulfates and carbonates of the Cambrian section in the Irkutsk Amphitheater. (1) Samples from the Angara Formation, (2) samples from the lower portion of the Cambrian section.

ratio if the Sr content is high (Vinogradov, 2003; Halverson et al., 2006). Figure 4 demonstrates the dependence of the measured Sr isotope ratio in carbonate and sulfate rocks of the Angara Formation on the Sr content in samples. The Sr contents in carbonates and sulfates show a very wide variation range (from tens to hundreds of times). Judging from Fig. 3, the Vendian/Cam-

brian boundary corresponds to $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.7080$, whereas the Early/Middle Cambrian boundary corresponds to ~ 0.7088 (dashed line in Fig. 4). However, contrary to the expectations, Fig. 4 does not demonstrate any correlation between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and the Sr content. Moreover, similarly low $^{87}\text{Sr}/^{86}\text{Sr}$ values are recorded in the entire the section. We suppose that this feature may be related to a partial averaging of the Sr isotope ratio in the section and the consequent decrease of the $^{87}\text{Sr}/^{86}\text{Sr}$ value in rocks.

Nevertheless, the terrigenous component of marlstones could be the main source of contamination of the sulfate-carbonate fraction of the section with radiogenic Sr. This is evident from the Rb-Sr data on the insoluble residue of marlstones (Table 2; Fig. 5).

Data points of insoluble residues of the Angara marlstone in the $^{87}\text{Sr}/^{86}\text{Sr}$ - $^{87}\text{Rb}/^{86}\text{Sr}$ diagram (Fig. 5a) are well approximated by a straight line. If one point is omitted, the slope of this line corresponds to the age of 515 ± 15 Ma and the initial ratio of 0.7085 ± 0.0006 (MSWD = 5).

Data points related to the insoluble residue of marlstone samples from Borehole 54 (Fig. 5b) yield a more complex pattern. The majority of samples lie within an angle limited by the boundary straight lines with slopes corresponding to 520–490 Ma. Three points (open circles in Fig. 5b) were omitted from calculations. These samples cover an approximately 100-m-long interval in

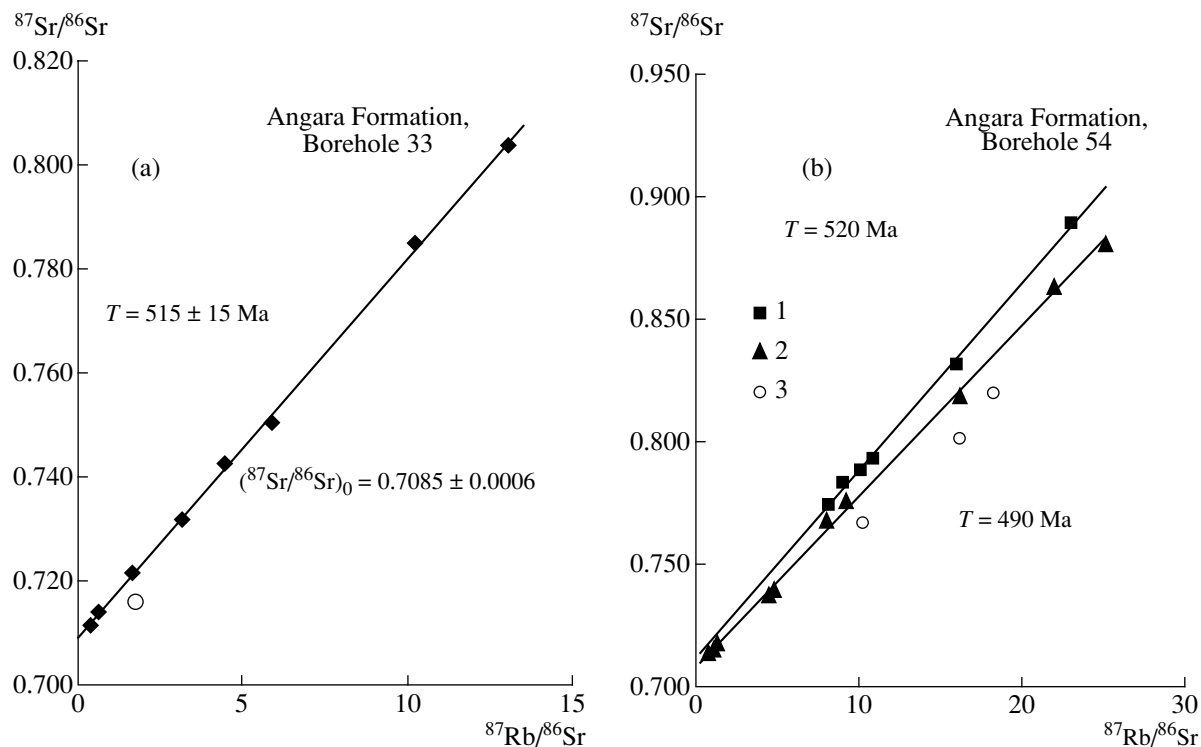


Fig. 5. Results of Rb-Sr measurements of insoluble residues of marlstones from the Angara Formation: (a) Borehole 54, (b) Borehole 33. (1, 2) tentative two rock groups used for the calculation of errorchrons; (3) samples omitted from calculation.

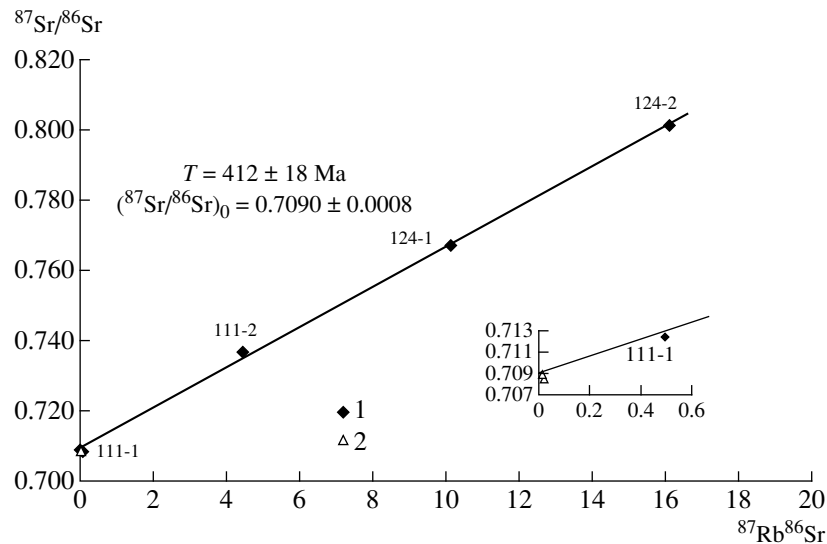


Fig. 6. Results of replicate Rb–Sr measurements in samples 111 and 124, Borehole 54. (1) Insoluble residue of marlstone, (2) carbonate fraction of marlstone.

the borehole section probably characterized by special conditions of disturbance of the Rb–Sr system in rocks.

It cannot be ruled out that the age of a real event (or a series of events close to the timing of sedimentation) is recorded in the insoluble silicate residues of marlstones.

The lowest age estimates were obtained from the results of Rb–Sr measurements in fractions of two marlstone samples (111 and 124). These samples were treated twice with hydrochloric acid (replicate runs). When washing out the carbonate fraction of marlstone, it is essential to avoid contamination with the silicate component (correspondingly, carbonate with radiogenic strontium). It is difficult to standardize this procedure. Therefore, location of four data points of the insoluble residues on a straight line (Fig. 6) may be attributed to the mixing of carbonate and silicate strontium species with the prevalent contribution of the silicate Sr of marlstones. Calculation based on four data points yields an age of $405 \pm 15 \text{ Ma}$ and initial $^{87}\text{Sr}/^{86}\text{Sr} = 0.7098 \pm 0.0012$. Calculation based on six data points (with allowance made for carbonates) yields $412 \pm 18 \text{ Ma}$ and $^{87}\text{Sr}/^{86}\text{Sr} = 0.7090 \pm 0.0008$. Hence, the calculated age of $\sim 410 \text{ Ma}$ is not accidental and corresponds to a certain event pertaining to the reworking of rocks. The reworking could be provoked, for example, by illitization of the clayey component owing to the input of K (and its chemical analogue Rb) from the host rocks. We can suppose that this process (“potassic metasomatism”) could be differently developed in various parts of the section.

K–Ar. Results of the K–Ar measurement in whole-rock mudstone samples from Vendian rocks of the Ushakovka and Moty formations (Table 3) also support the validity of Rb–Sr age estimates of potassic alteration.

Scatter of the calculated values is rather wide (Fig. 7). The slope of approximating lines yield the most probable age of 440–470 Ma. The upper intercept indicates that the samples contain ^{40}Ar excess, which is not supported by potassium.

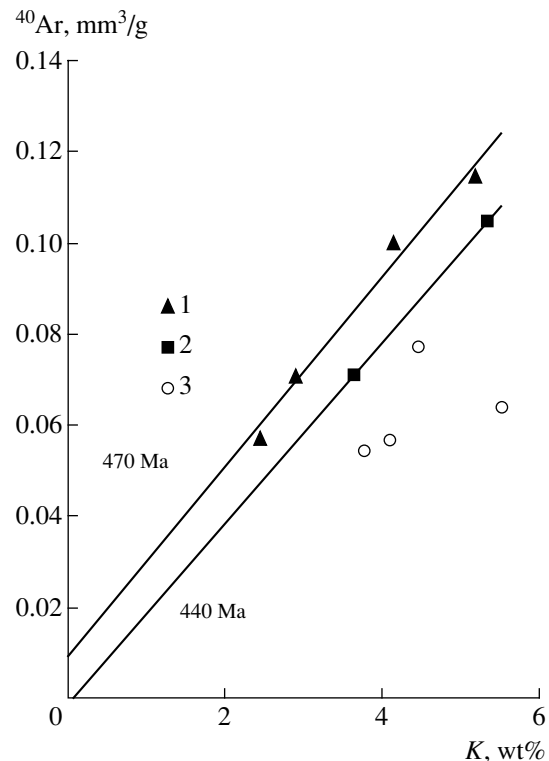


Fig. 7. ^{40}Ar vs. K relationship. (1) Samples with excess Ar; (2) samples without excess Ar, (3) samples with ambiguous K–Ar data.

Table 3. Results of K–Ar measurements in mudstones from the Ushakovka and Moty formations, boreholes Bel'sk and Zhigalovo

Sample no.	Depth, m	$^{40}\text{Ar}_{\text{rad}}$, mm ³ /g	K, wt %	Age, Ma
Borehole Zhigalovo				
2239	2506	0.0542	3.77	337
2318(b)	2620	0.0641	5.51	277
2319	2621	0.1143	5.18	494
2322	2624	0.1046	5.33	444
2238	2649	0.1000	4.15	533
Borehole Bel'sk				
1730	1708	0.0711	3.64	443
2077	1875	0.0707	2.89	540
2106	1888	0.0571	2.43	521
2184	1921	0.0569	4.10	326
2188	1922	0.0773	4.45	399

Note: Location of sample in the section is shown in Fig. 2 (Vinogradov et al., 2006b).

Sulfur. The bar chart in Fig. 8 summarizes all available data on the sulfur isotopic composition of Lower Cambrian sedimentary rocks from the Irkutsk Amphitheater (Vinogradov et al., 2006a; Vinogradov and Pustyl'nikov, 1994). The $\delta^{34}\text{S}$ distribution throughout the section and in the Angara Formation is close to the normal pattern. The modal value is equal to $\sim 27\text{--}28\%$,

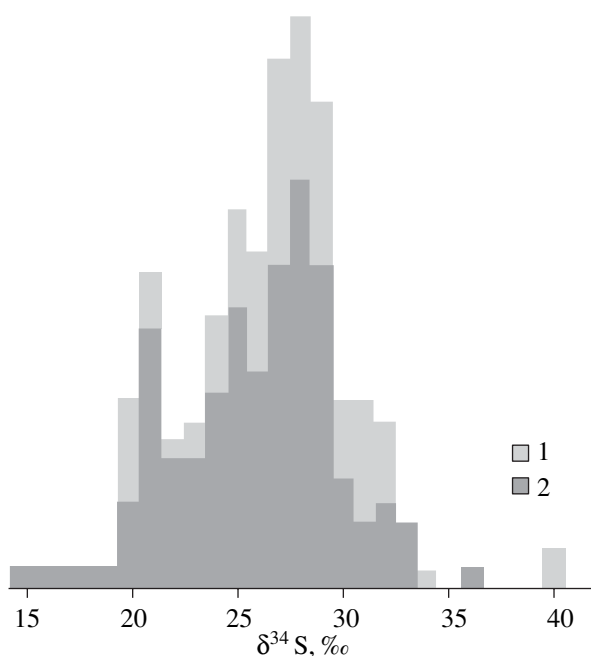


Fig. 8. Distribution of sulfur isotopic composition in anhydrite from (1) the lower portion of the Cambrian sequence and (2) the Angara Formation of the Irkutsk Amphitheater.

and this value is commonly ascribed to the sulfur of the Cambrian oceanic sulfate. However, the scatter of $\delta^{34}\text{S}$ values is so wide that we can rule out its random character. Obviously, this scatter reflects the well-known partition of sulfur isotopes in the course of sulfate reduction, when the residual unreduced sulfate is enriched in ^{34}S and the $\delta^{34}\text{S}$ value is higher. Therefore, in order to estimate the initial sulfur isotopic composition in water of sedimentary basin, it is more correct to take into account the left side of the bar chart limited by an interval of $\sim 15\text{--}22\%$. The additional peak near $\sim 22\%$ (Fig. 8), probably, corresponds to the initial composition. All higher $\delta^{34}\text{S}$ values should be regarded as indications of the participation of sulfur in sulfate reduction. This process cannot be referred to the time of sedimentation or early diagenesis. Although sulfate reduction undoubtedly proceeds at all stages of the formation and existence of rocks, the accumulation of a substantial amount of sulfates enriched in the heavy sulfur isotope is impossible. Therefore, the enormous amounts of such sulfates in nature could only be deposited at the epigenetic stage with the involvement of huge volumes of gypsum and anhydrite in sulfate reduction.

The undoubted reality of large-scale reduction in the studied sequences is supported by results of the detailed litho geochemical investigation reported in (Vinogradov, 2006a). Light hydrocarbons (mainly, methane) are the most probable reducers:



According to this reaction, one volume of anhydrite yields approximately 0.8 volume of calcite if the whole volume of CO_2 is fixed as the secondary CaCO_3 (Worden et al., 1996). Carbon of methane is commonly enriched in ^{12}C relative to the carbonate-hosted methane. Therefore, the participation of methane in sulfate reduction may transform isotopic systems of carbonate rocks in the section.

Carbon and oxygen of carbonates. Carbonate rocks of the Angara Formation were studied in Borehole 33. Levels of sampling for the determination of carbon and oxygen isotopic compositions are shown in Fig. 2; results of the isotopic study, in Table 4. All the data are summarized in Fig. 9. In the majority of samples, the carbon and oxygen isotopic compositions are close to the normal value, which is commonly inherent to the unaltered or slightly altered sedimentary carbonates. Only a few samples are enriched in the light carbon isotope ($\delta^{13}\text{C}$ up to -2.8%).

Thus, like rocks from the lower part of the Cambrian section, carbonates from the Angara Formation do not show any significant departures in the carbon and oxygen isotopic compositions toward positive or negative values (Vinogradov et al., 2006c). At the same time, two groups of samples from Borehole 33 demonstrate a clear inverse correlation between isotopic compositions of carbon and oxygen. Points of interrelated $\delta^{13}\text{C}$ and

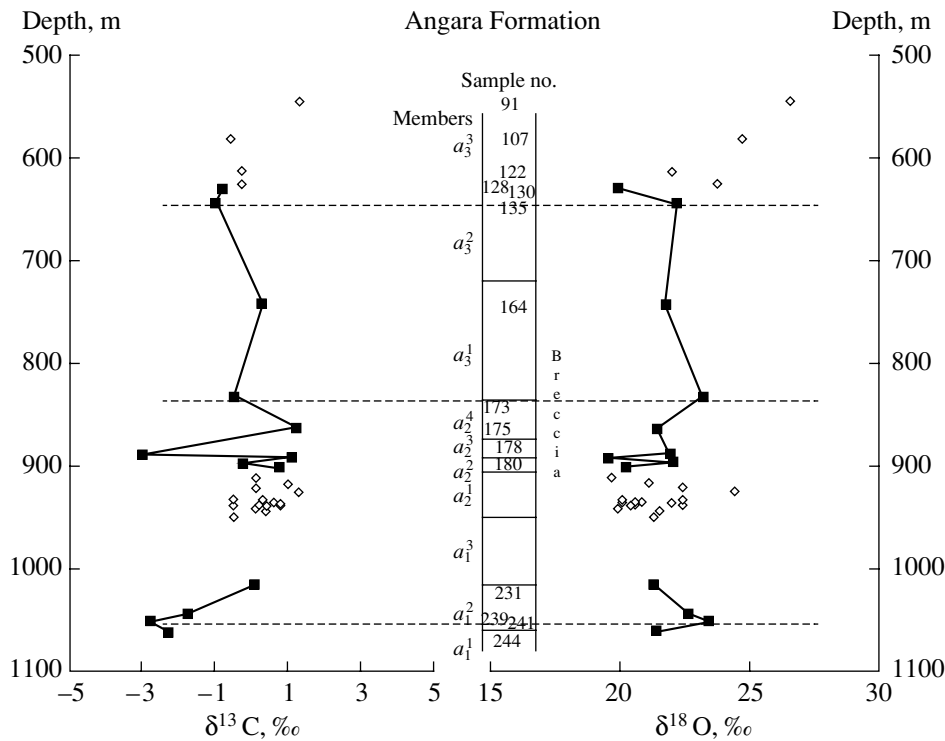


Fig. 9. Carbon and oxygen isotopic compositions in carbonates from the Angara Formation, Borehole 33.

$\delta^{18}\text{O}$ values are connected with tie lines in Fig. 9. The upper group of points within a depth interval of 600–900 m corresponds to the samples from solution breccia and overlying rocks of largely dolomitic composition, while the lower group is close to the base of the Angara Formation. Interrelation of carbon and oxygen isotopic compositions, low $\delta^{13}\text{C}$ values in these sample groups, and location of the upper group in the section testify to the secondary alteration of isotopic systems of carbonates. The absence of such relationships in other groups of samples does not rule out the reworking of rocks. As was repeatedly mentioned, the reworking is evident from the lithochemical observations.

One can see a certain contradiction between the considered data and their interpretation. The epigenetic reworking of carbonates should seemingly lead to their enrichment in the light carbon isotope (i.e., decrease in $\delta^{13}\text{C}$ value). Sulfate reduction and oxidation of methane or other organic reducers produce carbon dioxide enriched in the light carbon isotope. The carbon isotopic composition of methane generated at a depth of 1.5–2.0 km is characterized by $\delta^{13}\text{C}$ values ranging from approximately -35 to -40‰ (Galimov, 1968, 1973). Precisely this type of carbon isotopic composition is recorded in methane from the Markov field in the Irkutsk Amphitheater (Galimov, 1973). In oils from marine sediments, the $\delta^{13}\text{C}$ value ranges from -22.0 to -32.0‰ (Galimov, 1973; Eremenko et al., 1974; Kontorovich et al., 2005); in oils from the Angara–Lena and

Nepa–Botuoba petroliferous provinces, from -33.0 to -34.0‰ (Kontorovich et al., 2005).

Carbon dioxide, a product of hydrocarbon oxidation, should also have the same carbon isotopic composition. It is evident that CO_2 with such isotopic composition (hereafter, organic CO_2) should participate in the formation and transformation of carbonate rocks in the studied section. Shift in the isotopic composition of carbonate carbon will depend on quantitative proportions of carbonate and organic CO_2 . Judging from the average $\delta^{34}\text{S}$ value in sulfate sulfur, approximately 25–30% of the initial amount of sulfates in the section (i.e., ~100 m of anhydrite) was reduced (Vinogradov et al., 2006c). This estimate corresponds to ~1/5 of the total thickness of the Cambrian carbonate sequence in the Irkutsk Amphitheater. This proportion may shift the carbon isotopic composition averaged throughout the section by ~ 5 – 6‰ toward the enrichment of carbonates in ^{12}C (if the complete use of organic CO_2 is taken into consideration).

However, it is known that the initial ^{34}S value varies from $+4$ to $+8\text{‰}$ in carbonates deposited under conditions of high bioproductivity of water reservoirs and, especially, evaporitic basins (Botz and Müller, 1987; Magaritz and Stemmerik, 1989; Peryt and Magaritz, 1990; Kuleshov and Zhegalo, 1997; Bruckschen et al., 1999; Mayere and Schwar, 1999; Mii, 2001; Immenhauser et al., 2003; Jens et al., 2004). Therefore, the $\delta^{13}\text{C}$ values close to those in normal marine sediments

Table 4. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in carbonates from the Angara Formation, Borehole 33

Sample	Depth, m	$\delta^{13}\text{C}$, ‰	$\delta^{18}\text{O}$, ‰
91	544	1.3	26.5
107	580	-0.6	24.7
122	612	-0.3	22.0
128	624	-0.3	23.7
130	628	-0.8	19.9
135	643	-1.0	22.2
164	742	0.3	21.7
173	831	-0.5	23.2
175	862	1.2	21.4
178	887	-3.0	21.9
180	890	1.1	19.5
183	892	-0.2	22.0
184	895	0.8	20.2
185	896	0.1	19.7
187	901	1.0	21.1
190	910	0.1	22.4
199	924	1.3	24.4
203	932	-0.5	20.1
204	932	0.3	22.4
206	934	0.6	20.8
207 c	935	0.2	20.1
207 dol	935	0.8	20.6
208	935	0.8	22.0
209	937	0.8	22.4
209a, c	937	-0.5	20.4
209a, dol	937	0.4	20.6
210	940	0.1	19.9
212	943	0.4	21.5
215	949	-0.5	21.3
231	1016	0.1	21.3
239	1044	-1.7	22.6
241	1052	-2.8	23.4
244	1061	-2.3	21.4

Note: (c) Calcite; (dol) dolomite. See Fig. 2 for sample location in the section.

(0 ± 2) obtained in of our investigation may actually characterize metasomatically altered carbonates (Vinoogradov et al., 2006c).

It should also be kept in mind that not the whole amount of organic carbon dioxide participates in the reworking of rocks. A significant amount of CO_2 is removed from the rocks in gaseous and dissolved forms. Thus, the isotopic shift, relative to the initial isotopic composition of rocks, may be less.

Interpretation of the data on oxygen isotopic composition is still less definite. First, it is difficult to forecast oxygen isotopic composition in the primary rocks. It is assumed that the highest $\delta^{18}\text{O}$ values among the measured ones are close to the primary isotopic composition. The secondary processes, which are commonly related to the interaction of carbonate rocks with groundwaters of surface recharge, should decrease $\delta^{18}\text{O}$ values in carbonates. This is the common scenario. At the same time, groundwaters may contain organic CO_2 . Therefore, the positive correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in carbonates is regarded as an indicator of their secondary alteration. Inverse correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ recorded in a number of samples requires a more complex explanation that is beyond the scope of this paper.

CONCLUSIONS

Possibilities of the isotopic dating of ancient sedimentary rocks are very limited. In some cases, we can date the stages of rock transformation. However, uncertainties of such determinations are commonly very large. Therefore, special substantiations are always required to make sure that the calculated age values actually characterize some real episodes in the geological history of rock complexes under consideration. We attempt to look for such substantiations in the results of isotopic studies and only then correlate them with geological data.

The calculated age of the silicate fraction of the Angara marlstone ranges from 520 to 490 Ma and may imply that the rocks underwent compositional transformation approximately at this time interval. It cannot be ruled out that the last response of the Rb–Sr system of marlstones to geochemical transformation of rocks occurred 430–400 Ma ago (Fig. 6). In our opinion, this suggestion is supported by the K–Ar data on the Lower Cambrian shales, the transformation of which completed approximately at this time (Fig. 7).

Table 5 presents results of the calculation of pair correlation between the soluble fractions and insoluble residues of the Angara marlstone. Naturally, these results virtually coincide with data the on silicate component of marlstones.

The results obtained are consistent with geotectonic data. The southern and eastern parts of the Irkutsk Amphitheater are framed by the Salairian–Caledonian folding zones of the Central Asian Foldbelt. This region was marked by extremely intense tectonomagmatic–metamorphic events in the time span considered above in the course of active interactions with a promontory of the Siberian continent sandwiched between the folding zones. These events were responsible, in particular, for the most important episodes of thrusting and folding in both the basement and sedimentary cover. This is evident from the results of geological–geophysical surveys and drilling performed during the last decades.

Table 5. Results of calculation of Rb–Sr age for marlstone fractions from the Angara Formation, Borehole 54

Sample no.	Number of points	Age, Ma	$(^{87}\text{Sr}/^{86}\text{Sr})_0$
29	3	460 ± 20	0.7088 ± 0.0009
39	5	535 ± 30	0.7085 ± 0.0008
70	2	490	0.7085
86	5	430 ± 35	0.70853 ± 0.0003
111	5	440 ± 20	0.7084 ± 0.0004
124	5	406 ± 5	0.7085 ± 0.0002
163	2	479	0.7077
167	2	535	0.7091
169	3	555 ± 20	0.7090 ± 0.0010
171	2	551	0.7084

Note: See Fig. 1 and Table 2 for sample location in the section and for analytical data.

These works are considered in works of M.M. Maldenbaum, A.V. Migurskii, V.S. Starosel'tsev, B.A. Sokolov, V.I. Sizykh, N.L. Dobretsov, G.G. Shemin, and others. A review of these data is given by Sizykh (2001). They revealed a wide belt of tectonic nappes extending along margins of the Siberian Platform as a continuation of more vigorous thrusting in the adjacent foldbelts. Toward the central Irkutsk Amphitheater, this belt gave way to the belt of frontal thrusts and the reflected supra-frontal structures (Sizykh, 2001). The formation of such foldbelts fostered not only the displacement of huge rock masses but also the large-scale migration of all types of fluids. Let us emphasize once again that the study territory is located precisely in such a region.

Thus, the data obtained indicate that tectonic events mentioned above are also imprinted in the platformal environment as distinct litho geochemical features related to significant displacements of rock masses and the migration of chemical elements recorded in the isotope data.

According to the alternative view, the marginal platform zones, which adjoin the Early Paleozoic Foldbelt, "were not affected by any appreciable tectonic, metamorphic, or magmatic reworking in the Vendian and Early Paleozoic" (Yarmolyuk et al., 2003, p. 357). The data presented above allow us to agree with this statement only with respect to magmatism and metamorphism. As concerns tectonic deformations and their geochemical consequences, this point of view should be subject to further discussion.

The widespread Mesozoic trap magmatism of the Siberian Platform is hardly reflected in isotopic systems of Cambrian rocks of the Irkutsk Amphitheater.

Samples used for the Rb–Sr reconstructions embrace the whole Lower Cambrian section. This implies that processes of reworking during a relatively short span of time affected the nearly 2-km-thick plat-

formal sedimentary sequence that represented an open system in geochemical and hydrogeological terms. The relatively open character of the system could promote a considerable averaging of the C, S, and Sr isotope ratios throughout the section. It cannot be ruled out that precisely the Early Paleozoic events triggered the main processes of dissolution and removal of salts and large-scale sulfate reduction, which are clearly recorded in the sulfur isotopic composition of sulfates.

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