

Isotopic Signatures of Deposition and Transformation of Lower Cambrian Saliferous Rocks in the Irkutsk Amphitheater: Communication 2. Strontium Isotopic Composition

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Abstract—Rb–Sr data were obtained for different Lower Cambrian rocks from boreholes Bel'sk and Zhigalovo drilled in the Irkutsk amphitheater. Shales in the lower part and insoluble residue of marls throughout the entire (up to 2 km thick) sequence define the first transformation stage of silicate rocks dated at 580 Ma with a large uncertainty. Sulfate and carbonate rocks are the main Sr carriers in the Lower Cambrian rocks. Owing to a negligible amount of silicate impurities in them, the input of radiogenic Sr exerted no significant influence on the Rb–Sr isotope system. However, almost all carbonate and sulfate rocks studied are contaminated by radiogenic Sr relative to its initial isotopic composition in the sedimentation basin. Hence, the rocks experienced epigenetic (probably, repeated) recrystallization and one or several stages of dissolution.

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INTRODUCTION

In our first communication based on sulfur isotope data, we showed that all rocks of the almost 2-km-thick Lower Cambrian saliferous sequence of the Irkutsk amphitheater experienced intense secondary alterations (reduction of thickness and chemical and mineral transformations). The alterations primarily affected the sulfate part of rocks. Most anhydrites were removed in the course of sulfate reduction accompanied by the recrystallization of anhydrites and carbonate rocks of the section. Evidence of dissolution, redeposition, and recrystallization of halite, anhydrite, and carbonates is distinctly defined by lithological methods (Pisarchik, 1963; Pisarchik *et al.*, 1975). Alterations mentioned above suggest the regional inundation and permeability of rocks. These features of rocks are also indicated by hydrogeological (Pinneker, 1966) and geothermic investigations (Lysak and Zorin, 1976).

The aim of this work was to determine the influence of secondary epigenetic alterations on the Rb–Sr isotope systems of different Lower Cambrian rocks. We used samples from the same sections of boreholes Bel'sk and Zhigalovo that were used in the previous sulfur isotope study.

METHODS

Strontium isotopic composition was determined using a double Re-filament on a Finnigan MAT-260 mass spectrometer. The $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio was calculated from the isotope dilution analysis. Results were normalized to $^{88}\text{Sr}/^{86}\text{Sr} = 8.37521$ and corrected for the VNIIM CaCO_3 standard with $^{87}\text{Sr}/^{86}\text{Sr} = 0.70802$ (Vinogradov and Chernyshev, 1987). The average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (based on 11 measurements) is 0.70815 ± 0.0002 . Errors in the measurement of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ were no more than ± 0.0002 and $\pm 1\%$, respectively.

Bulk samples of clayey rocks from the lower part of the section were treated by the conventional technique: powdered samples ($\sim 200 \mu\text{g}$) were decomposed in the ($\text{HF} + \text{HNO}_3$) solution supplemented with the ($^{87}\text{Rb} + ^{84}\text{Sr}$) tracer (Vinogradov *et al.*, 2002). Carbonates were preliminarily washed in an ultrasonic bath and dissolved in 1 N HCl. After the removal of carbonates and anhydrites, the insoluble residue was centrifuged and decomposed as normal clayey rocks.

GEOCHEMICAL SIGNIFICANCE OF STRONTIUM ISOTOPE RATIOS IN SEDIMENTARY ROCKS

Study of the Rb–Sr isotope system makes it possible to date the formation or transformation of rocks and to establish some specific features of their geochemical evolution.

Dating of clastic sedimentary rocks is mainly complicated by their initial heterogeneity and preservation of their provenance memory. Isochron model used in the Rb–Sr method is based on homogenization of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio over the entire volume of studied object (such a homogenization is the main subject of dating). It is hardly possible to fulfill this condition in sedimentary rocks. Another essential condition for the validity of isochron model—closure of isotope system during subsequent events—is even more problematic for sedimentary rocks. Therefore, we can only estimate the age of sedimentary rocks with a high degree of uncertainty concerning the numerical expression and geological interpretation of relevant event. These problems were repeatedly considered in literature, in particular, in one of the latest detailed works supplemented with a voluminous bibliography (Rasmussen, 2005).

In accordance with specifics of the Sr isotope study of sedimentary rocks, the obtained data were treated with appropriate statistic methods, which took into consideration the fact that analytical errors are negligible with respect to uncertainties introduced by natural noise (geochemical dispersion). Errorchrons were constructed using methods described in (Bujakaite *et al.*, 2005). Isochron and errorchron were distinguished by the χ^2 method (Sokolov and Bujakaite, 1986), while the errors of considered linear dependences were estimated after (York, 1966). This approach does not use the notion of mean square weighted deviations (MSWD). However, we also calculated this value for the comparison with other estimates.

The geochemical significance of Sr isotope investigations is primarily related to deciphering $^{87}\text{Sr}/^{86}\text{Sr}$ evolution in the oceanic water. This ratio in the present-day ocean is constant (0.709) because of the prolonged residence of Sr (~5 Ma) in ocean as compared to the mixing time of oceanic waters (~1000 yr) and the significantly higher concentration of Sr in the ocean relative to its average content in the river water (Palmer and Edmond, 1989; Faure, 1986). Therefore, Sr isotope ratio in the oceanic water can be ascribed to the category of planetary constants that characterize conditions of Sr circulation for certain geological intervals. Variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in oceans during geological time depend on the share of continental Sr (on the average, 0.711) in the oceanic reservoir and Sr from bottom oceanic basalts (~0.703).

A vast number of works is devoted to the study of Sr isotopic composition in sedimentary carbonates. As usual, the main difficulty in isotope geochemistry is to prove that the Sr isotope system remained close since the sedimentation time. In most cases, secondary transformations of carbonate (and sulfate) rocks increase the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio owing to the contamination (via aqueous solutions) of carbonates by the more radiogenic Sr from silicate clastic rocks. Therefore, the lowest measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are typically applied to decipher the Sr isotope evolution in the ancient oceans. The $^{87}\text{Sr}/^{86}\text{Sr}$

evolution curves for oceanic water were constructed on the basis of these investigations (Jacobsen and Kaufman, 1999; Veizer *et al.*, 1999; Walter *et al.*, 2000; and others). Unlike sulfur, oxygen, and carbon, strontium is not subjected to natural physicochemical processes leading to isotope fractionation. Addition of ^{87}Sr owing to the radioactive decay of ^{87}Rb is the only cause for variation in the Sr isotopic composition. Therefore, the Rb–Sr system is more simple for interpretation than stable isotope systems (C, O, and S), and the Sr isotope curve best reflects the real state of isotope system in ancient sedimentation basins.

Precipitation together with Ca as carbonate or sulfate is the main mechanism of Sr removal from oceanic water. The Sr content in freshly precipitated carbonates is typically 0.n%. In some cases, the content may reach up to 1%, depending on a great number of hardly controlled factors (Wolf *et al.*, 1971), such as the Sr/Ca ratio in water and the total Sr content in the initial solution (consequently, the TDS content). Comparison of Sr isotope data on different rocks makes it possible to reconstruct their geological evolution.

STRONTIUM ISOTOPIC COMPOSITION OF LOWER CAMBRIAN ROCKS IN THE IRKUTSK AMPHITHEATER

The general lithological scheme of Cambrian rocks of the Irkutsk amphitheater is shown in Fig. 1.

Lower Cambrian rocks of the Irkutsk amphitheater and the remaining area of the East Siberian Craton are mainly composed of carbonates with a variable admixture of clay, rock salt, and anhydrites. Terrigenous rocks occur only in the basal part of the platform cover (Ushakovka and lower Moty formations). Figure 2 presents detailed lithological sections of both sampled boreholes. Results of Rb–Sr measurements are listed in Tables 1–3.

We studied all rock types (mudstones at the base of the Lower Cambrian section, anhydrite–dolomitic and dolomitic marls, carbonates, and sulfates).

Mudstones. Mudstones occur only in the Ushakovka and Moty formations at the base of the Lower Cambrian section in the Irkutsk amphitheater. Their precise stratigraphic assignment is unclear (Upper Vendian or Lower Cambrian). Positions and results of the analysis of bulk mudstone samples from the section are given in Fig. 2 and Table 1.

Isochron diagram based on 19 analyses (Fig. 3) shows that 18 data points define a band constrained by two straight lines with the same slope. Samples from different boreholes make up separate clusters. In particular, samples from Borehole Bel'sk (10 measurements) include 7 data points plotted near the upper curve that yields an age of 580 ± 40 Ma and initial Sr ratio of 0.723 ± 0.003 (MSWD = 11). Samples from Borehole Zhigalovo (9 measurements) include 6 data points plotted on the lower line that defines an age of 600 ± 40 Ma

System, period	Stage	Formation, thickness, m	Composition
ϵ_3		Verkhnyaya Lena 450–800	Sandstones, siltstones, and dolomitic marls (with anhydrites in the lower part)
ϵ_2	Maya		
	Amga	Angara 380–600	Dolomites, rock salt and anhydrites
ϵ_1	Lena	Bulai 120–145	Dolomites
		Bel'sk 300–450	Rock salt (in the upper part), dolomites, limestones and anhydrites
		Usol'e 600–1000	Rock salt dolomites, and anhydrites
V?	Aldan	Moty 300–400	Upper Middle Lower
		Ushakovka 100–500	Dolomites, marls, and anhydrites Dolomites, sandstones, anhydrites and marls Quartzose sandstones Sandstones, siltstones, and mudstones

Fig. 1. Lithostratigraphic scheme of Cambrian rocks of the Irkutsk amphitheater.

and initial Sr ratio of 0.710 ± 0.002 (MSWD = 9). It is worth mentioning that values calculated for both boreholes are similar. Hence, positions of data points in the plot are not related to accidental noise, and the linear trends have a geological meaning.

Marls. Marls extend over a significantly greater depth interval including Lower Cambrian rocks. Data on the clay component of marls are presented in Fig. 4 and Table 2.

In the isochron diagram (Fig. 4), data points from both boreholes define a common linear trend with a slope corresponding to 575 ± 30 Ma (MSWD = 30). This value is close to that obtained from shales. The initial $^{87}\text{Sr}/^{86}\text{Sr}$ is 0.709 ± 0.001 .

Carbonates and anhydrites. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the sedimentation environment can be estimated using the lowest measured values for anhydrites and carbonates that are the main Sr carriers in the studied rocks.

Carbonates (mostly, dolomites) sharply dominate in the section. They were dissolved in 1 N HCl. When they occur in mixture with anhydrite, some part of the latter

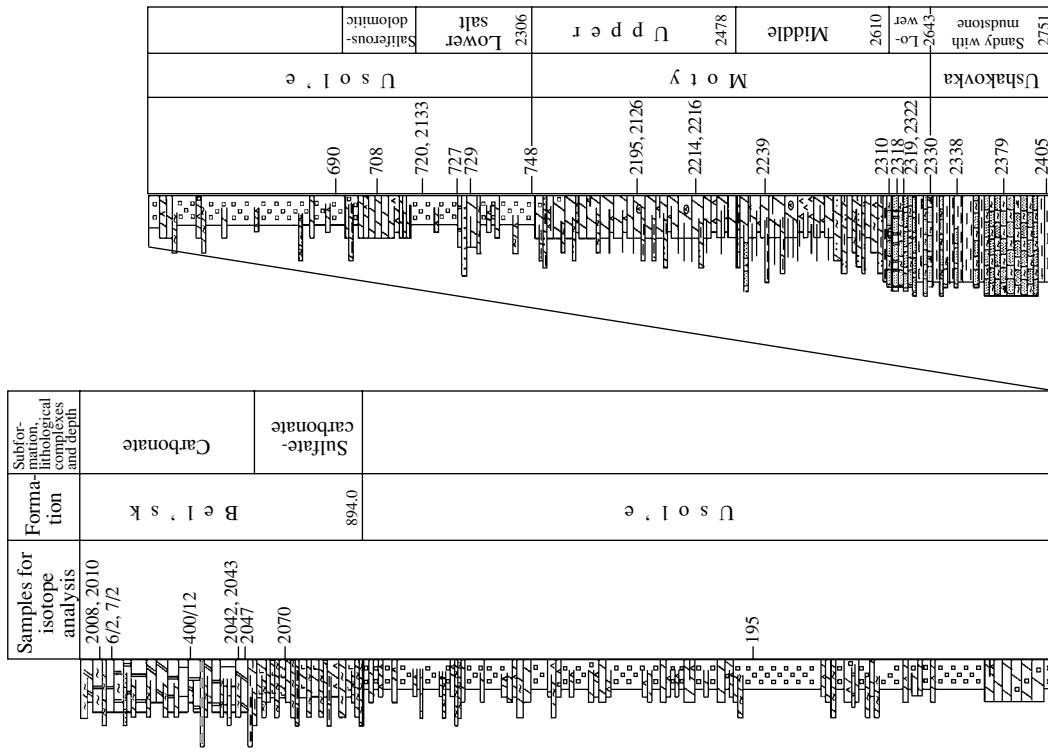
mineral can also be transferred to solution. The Sr content is typically higher than $500 \mu\text{g/g}$ in anhydrites and no more than $200 \mu\text{g/g}$ in dolomite. Therefore, samples with $>500 \mu\text{g/g}$ Sr are arbitrarily termed anhydrite (Table 3), although they represent anhydrite with dolomite admixture.

As seen in Table 3 and Fig. 5, Sr isotope ratios in sulfate and carbonate rocks demonstrate a large scatter from 0.7077 to 0.7100. No correlation is observed between the Sr isotope ratio and the stratigraphic assignment of samples.

DISCUSSION

Silicate material. Dates of 580 and 600 Ma tentatively calculated from silicate samples must be treated with caution. Primarily, the dates obtained on both boreholes are similar and consistent with the stratigraphic (Vendian) age scale. Therefore, one can suppose that positions of data points in Fig. 3 are actually governed by age. To test this assumption, we analyzed

Borehole Zhigalovo



Borehole Bel'sk

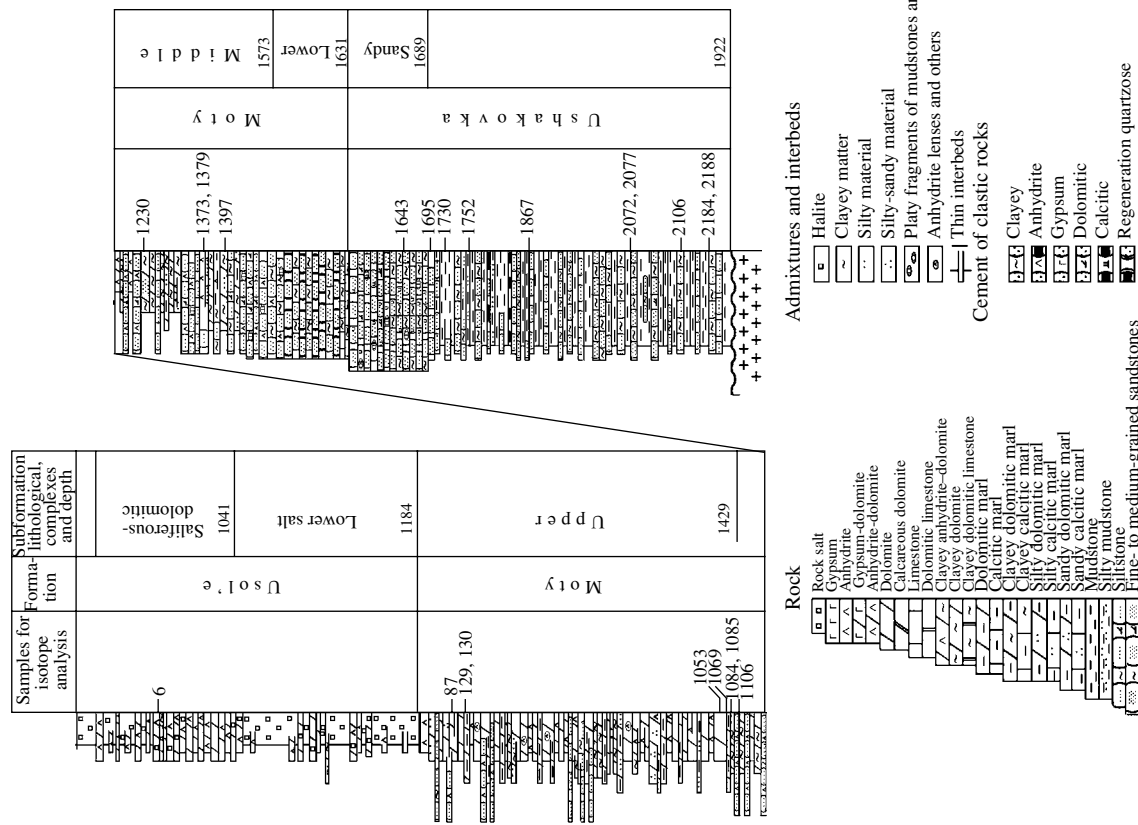


Fig. 2. Lithological columns of boreholes Bel'sk and Zhigalovo and Rb-Sr sampling localities.

Table 1. Rb–Sr isotope systems in mudstones

Sample no.	Sampling depth, m	Formation	Rb, $\mu\text{g/g}$	Sr, $\mu\text{g/g}$	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$
Borehole Bel'sk						
1643	1673	Ushakovka	103.7	105.7	2.85	0.74681
1695	1695	"	177.3	69.53	7.41	0.75372
1730	1708	"	94.72	63.01	4.37	0.75640
1752	1718	"	168.5	124.3	3.94	0.74602
1867	1775	"	158.0	54.79	8.41	0.79150
2072	1870	"	154.5	59.57	7.56	0.78510
2077	1875	"	138.8	51.33	7.89	0.78874
2106	1888	"	124.3	46.23	7.84	0.78966
2184	1921	"	200.9	57.97	10.12	0.80411
2188	1922	"	207.1	79.45	7.59	0.77589
Borehole Zhigalovo						
2239	2506	Moty	74.21	77.02	2.79	0.73236
2310	2603	"	113.9	180.0	1.833	0.72619
2318(b)	2620	"	163.6	95.0	5.01	0.75214
2319	2621	"	148.9	68.44	6.33	0.76540
2322	2670	"	143.4	72.81	5.73	0.75880
2330	2638	"	103.2	62.65	4.79	0.75048
2238	2649	Ushakovka	119.3	65.49	5.30	0.76302
2379	2701	"	84.70	66.03	3.73	0.74718
2405	2751	"	185.0	111.6	4.82	0.75732

Table 2. Rb–Sr isotope systems in the silicate component of marls

Sample no.	Sampling depth, m	Formation	Rb, $\mu\text{g/g}$	Sr, $\mu\text{g/g}$	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$
Borehole Bel'sk						
6	986	Usol'e	64.50	882.0	0.212	0.70984
130	1197	Moty	63.28	572.0	0.320	0.71174
1053	1424	"	113.7	26.81	12.86	0.80596
1069	1427	"	84.05	39.10	6.25	0.75980
1230	1475	"	72.91	119.3	1.771	0.72527
1379a	1527	"	138.0	76.55	5.24	0.75558
1397	1531	"	74.68	28.90	7.53	0.78662
Borehole Zhigalovo						
2008	511	Bel'sk	88.50	35.95	7.17	0.77138
2047	745	"	83.71	83.72	2.90	0.73270
2070	822	"	28.53	138.9	0.594	0.71318
195	1758	Usol'e	131.7	79.96	4.79	0.74438
690	2150	"	56.21	18.01	9.10	0.78484
2196	2418	"	125.5	23.16	15.87	0.83463

the clayey constituent of marls and obtained a similar date of 575 Ma.

Such a coincidence strongly supports the age interpretation of linear dependences mentioned above. The

low probability of accidental coincidence suggests that Rb–Sr data on the silicate material actually record a real event with an age of 580 Ma. Unfortunately, this value has a high uncertainty of ± 30 Ma.

Table 3. Rb–Sr isotope systems in carbonates and anhydrites

Sample no.	Depth, m	Rock	Rb, $\mu\text{g/g}$	Sr, $\mu\text{g/g}$	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$
Borehole Bel'sk						
Usol'e Formation						
6	986	Clayey dolomite–anhydrite rock	2.63	866	0.009	0.70825
Moty Formation, upper subformation						
87	1190	Anhydrite with thin interbeds of quartzose sandstone	2.19	882	0.007	0.70863
129	1196	Felted-fibrous anhydrite at the contact with sandstone	8.46	676	0.036	0.70868
130	1197	Clayey dolomite with lenslike anhydrite aggregates	6.40	1161	0.016	0.70877
1053	1424	Dolomitic silty marl with pyrite	18.85	182	0.300	0.70990
1069	1427	Dolomitic silty marl with pyrite and anhydrite interbeds	110.1	1200	0.266	0.70973
Moty Formation, middle subformation						
1084	1430	Dolomitic silty marl with anhydrite and pyrite lenses	1.43	700	0.006	0.70863
1085	1431	Felted-fibrous anhydrite	1.82	853	0.006	0.70871
1106	1437	Vaguely bedded anhydrite	6.82	1061	0.019	0.70868
1230	1475	Clayey dolomite with admixture of primary anhydrite and pyrite	2.70	399	0.020	0.70882
1373	1526	Anhydrite with dolomite veinlets and lenses of clay material	1.55	1078	0.004	0.70883
1379	1528	Clayey dolomite with anhydrite admixture	11.19	472	0.069	0.70965
1397	1531	Dolomitic marl with clay interbeds	4.62	60.6	0.221	0.71004
Borehole Zhigalovo						
Bel'sk Formation						
2008	511	Clayey dolomite	2.38	51.2	0.135	0.70935
2010	513	Calcareous dolomite with carbonate–clayey films	0.556	182	0.009	0.70853
6/2	517	Dolomitic limestone with carbonate–clayey films	3.69	170	0.063	0.70887
7/2	521	Dolomitic limestone with sutures	0.253	99.7	0.007	0.70800
400/12	665	Strongly recrystallized limestone with sutures	6.87	189	0.105	0.70833
2042	717	Dolomitic limestone	0.525	195	0.078	0.70839
2043	724	Dolomitic marl with quartz–mica aleurites	0.874	54.9	0.046	0.70840
2047	746	Clayey silty dolomite	8.76	193	0.132	0.70851
2070	822	Dolomitic marl with gypsum veinlet	0.607	85.1	0.021	0.70799
Usol'e Formation						
195	1758	Salinated clayey dolomite	3.17	190	0.048	0.70870
690	2151	Clayey silty dolomite	1.31	104	0.036	0.70768
708	2176	Recrystallized dolomite	0.148	47.8	0.009	0.70814
720	2237	Salinated dolomitic limestone with anhydrite	0.566	119	0.014	0.70807
2133	2238	Dolomitic limestone with halite (calcitic part)	0.856	140	0.018	0.70797
2133	2238	The same, dolomitic part	3.11	120	0.075	0.70830
Moty Formation, upper subformation						
748	2307	Dolomite with halite	2.01	45.8	0.127	0.70887
2195	2413	Dolomite with anhydrite inclusions	1.24	74.7	0.048	0.70861

Errorchron dependences can also be interpreted as mixing lines. One end member may be represented by some silicate matter introduced from provenance, while the other member may be represented by strontium from sulfate–carbonate rocks. To preserve the linear

trend in the course of mixing, silicate component transported from a vast area must have the similar age over the entire sampled 2-km-thick section. It is difficult to image the supply of such isotopically homogeneous but unequigranular material into sedimentation basins,

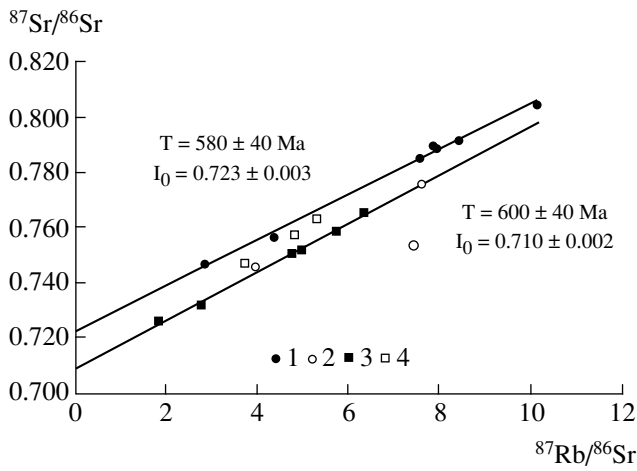


Fig. 3. Rb–Sr isochron diagram for mudstones of the Moty and Ushakovka formations. (1, 2) Borehole Bel’sk; (3, 4) Borehole Zhigalovo; (2, 4) samples omitted from errorchron calculations.

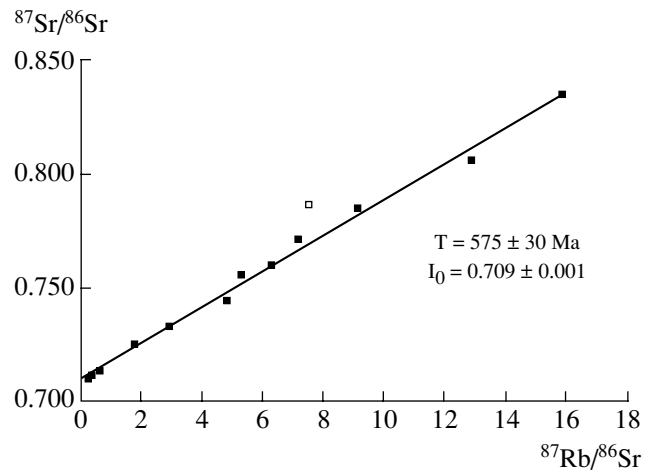


Fig. 4. Rb–Sr isochron diagram for silicate component of the Lower Cambrian marls (boreholes Bel’sk and Zhigalovo). Open box designates sample omitted from errorchron calculations.

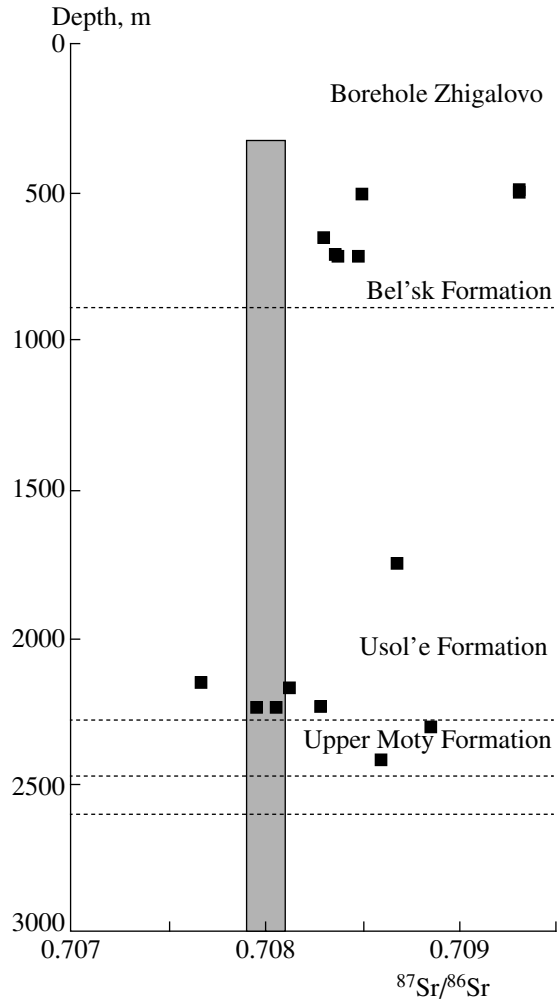
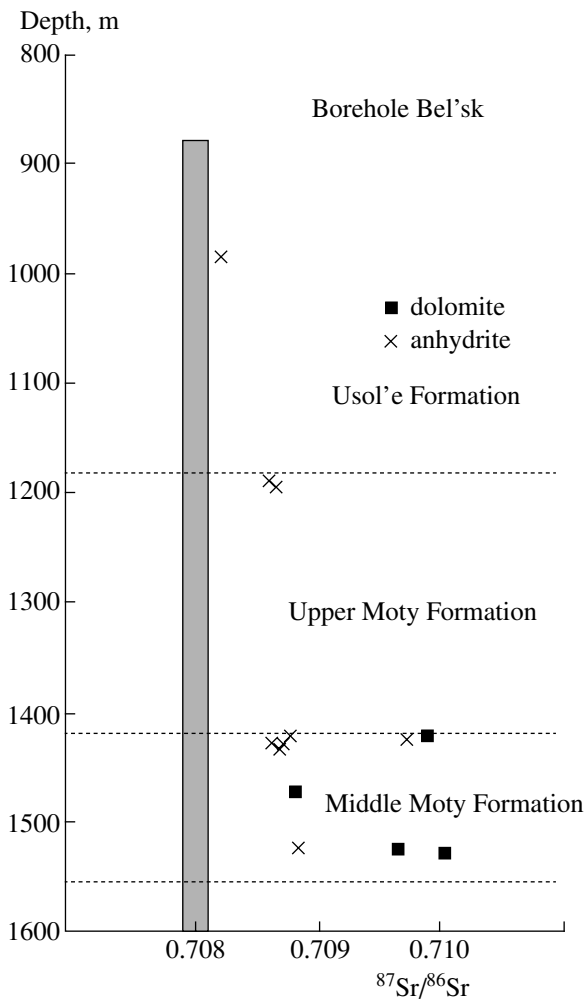


Fig. 5. Variations of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in dolomites (including the carbonate part of marls) and anhydrites from boreholes Bel’sk and Zhigalovo.

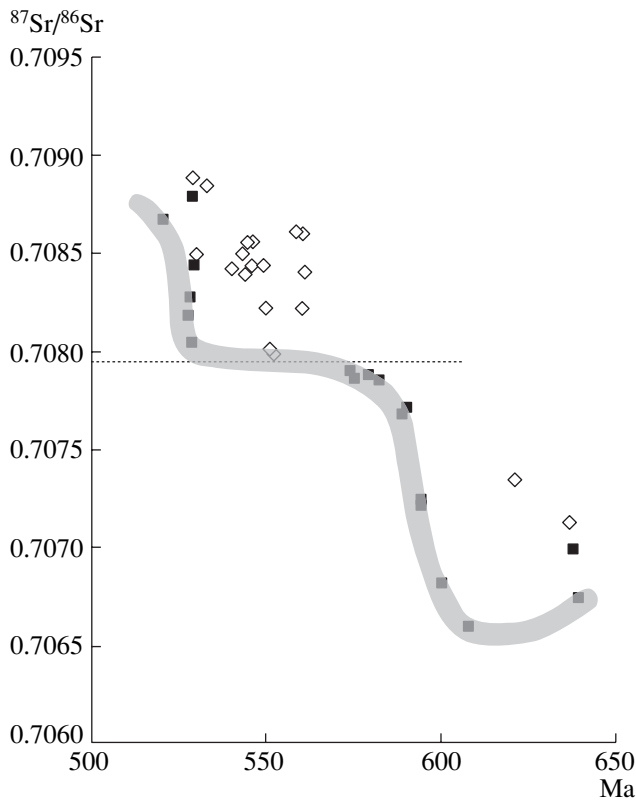


Fig. 6. Sr isotopic composition of seawater in the Vendian–Lower Cambrian. Filled boxes are the most representative samples. Modified after (Walter *et al.*, 2000).

since the thick sedimentary sequence was accumulated over a long period in distant areas. In addition, shales from two boreholes have sharply different initial Sr ratios: 0.710 for samples from Borehole Zhigalovo and 0.723 for Borehole Bel'sk. Hence, in the case of mixing line, the low-Rb components should be different for both boreholes and unique circumstances should be required for holding the parallel positions of the slopes. At the same time, their age interpretation implies the existence of some event that was responsible for the transformation of rocks and homogenization of the Sr isotopic composition in the rock body. We realize that the estimated time of epigenetic event is inconsistent with the currently accepted age estimate for the Vendian–Cambrian boundary (Semikhatov, 2000).

Chemogenic material. Carbonates and anhydrites are the main Sr carriers. Therefore, they are commonly used to reconstruct the Sr isotope evolution of seawater.

Figure 6 constructed from data reported in the overview (Walter *et al.*, 2006) presents the measured Sr isotopic composition of Vendian–Cambrian carbonates in the world. Based on low $^{87}\text{Sr}/^{86}\text{Sr}$ values that are least altered by secondary processes, the most probable Sr isotope ratio in seawater at interval of 480–590 Ma is $\sim 0.7080 \pm 0.0001$.

Estimates mentioned above are among the lowest values obtained for chemogenic rocks. Therefore, one can suppose that these (or lower) values were typical of seawater in sedimentation basins of the Vendian–Cambrian time. Most part of the studied anhydrites and dolomites have higher Sr isotope ratios, indicating the contamination of these rocks by radiogenic Sr during secondary alterations. It is interesting that the shift of Sr isotopic composition in anhydrites, which are most enriched in Sr, is similar to that in the significantly less enriched dolomites. This is presumably related to the high solubility of anhydrite and its lower resistance to secondary processes. In addition, virtually all anhydrite samples were taken from Borehole Bel'sk located at the border of the Irkutsk amphitheater, where reworking could be stronger than in the central part (Borehole Zhigalovo).

In the overwhelming majority of cases, the samples are contaminated by radiogenic Sr that could be derived from terrigenous component of the section and potassium salts. The samples could only be contaminated through solutions. Thus, the available material again confirms that virtually all carbonate and sulfate rocks of the section experienced dissolution and recrystallization.

CONCLUSIONS

(1) Interaction of rocks of virtually the entire Lower Cambrian section with aqueous solutions was responsible for the shift of their primary Sr isotope ratios.

(2) At least one stage of this reworking was temporally close to the timing of not only chemogenic, but also silicate and carbonate rocks. These transformations are also distinctly expressed in other (primarily, sulfur) isotope systems of saliferous rocks of the Irkutsk amphitheater (Vinogradov *et al.*, 2006).

(3) Sr isotopic composition in silicate component of marls also changed over the entire sampling interval (1400 m) 575 ± 30 Ma ago. Within uncertainty limits of the dating method, the above value coincides with the timing of shale transformations. The chemogenic part of the section could change gradually or by stages during the entire lifetime of the rock. Sr isotope ratios in anhydrites and carbonates are generally higher than the inferred Sr isotope ratio in seawater of sedimentation basins.

(4) In some cases, the Rb–Sr system retained low $^{87}\text{Sr}/^{86}\text{Sr}$ value (~ 0.708) inferred for seawater of sedimentation basins.

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