

The Strontium Isotopic Composition in Glendonites of the Middle Jurassic in Northern Siberia

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Abstract—The Sr isotope composition in glendonites from two sections of the Middle Jurassic of Northern Siberia has been determined for the first time. Glendonite was formed by the replacement of icite by calcite during diagenesis. The $^{87}\text{Sr}/^{86}\text{Sr}$ in most of the samples of glendonites (0.70687–0.70715) is insignificantly lower than this ratio in the Late Bathonian–Early Bajocian ocean. This may indicate a contribution from the Callovian seawater in the formation of individual calcite generations or the influence of methanogenic fluid of deep origin.

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Glendonites, stellate or bipyramidal calcite occur widely in the Middle Jurassic (Bajocian–Bathonian) sediments of Northern Siberia [1–3]. The glendonites are pseudomorphs of calcite after ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$), formed under the action of methanogenic carbon dioxide at low temperatures ($<5\text{--}8^\circ\text{C}$) [1–3]. The rapid transformation of ikaite into glendonite and the high content of Sr in glendonites [1, 4] suggest that glendonites retain the primary isotope ratio of the sedimentary environments, which opens the possibility to apply the strontium isotope stratigraphy (SIS) method.

During the Middle Jurassic, a high rate of decrease of $^{87}\text{Sr}/^{86}\text{Sr}$ in the ocean occurred: it reached a minimum at the turn of the Middle and Late Jurassic. The maximum rate of change of this ratio for the Phanerozoic was found for the Bajocian [5]. This makes strontium isotope stratigraphy (SIS) a promising tool for comparing the Bajocian–Bathonian marine deposits, which is especially important because of the difficulties of Boreal–Tethyan correlation in this interval using solely biostratigraphic data. The main material for SIS in the Precambrian is sedimentary carbonate rocks [6], while in the Mesozoic, mainly carbonate shells and belemnites are used [5, 7], along with samples of carbonate rocks [8].

The Middle Jurassic marine sediments in the north of Siberia form a sequence of interbedding silts, clays, and sands. Belemnites, often used for SIS purposes, are relatively sparse here. The mollusk fauna is dominated by bivalves, predominantly of the boreal genera *Retroceramus* and *Arctotis*. The glendonites are found at all stages and substages of the Middle Jurassic of Siberia, but they are most abundant in the Bajocian–Middle Bathonian interval. The glendonite samples for this study were collected from two sections (Fig. 1). The reference section located on the shores of Anabar Bay is one of the most studied sections of the Lower Middle Jurassic in the region [9]. Glendonites were found here at different stratigraphic levels (Fig. 1). In the section on the Lena River, located at Kystatym Cape [10], numerous glendonites occur in a narrow stratigraphic interval. Additionally, for the purpose of comparison, the strontium isotope composition of the Holocene glendonites [11], collected on the littoral of the White Sea, was studied.

An X-ray study, performed employing a DRON-UM-1 diffractometer (Cu radiation, $2^\circ/\text{min}$), showed that all the samples of glendonites are composed of calcite. The position of the most intense peak (3.03 \AA) in the diffraction pattern of the mineral corresponds to the hkl (104) calcite reflex. This confirms the complete replacement of the original ikaite in both the Mesozoic and Holocene sediments.

Determination of the concentrations of Mg, Mn, and Fe was carried out by the atomic-emission method using an ICPE-9000 spectrometer (Research Park, St. Petersburg State University). Chemical treatment of the glendonite samples for isotopic analysis included preliminary ultrasonic washing of the pulverized sample (50 mg) in purified water and sub-

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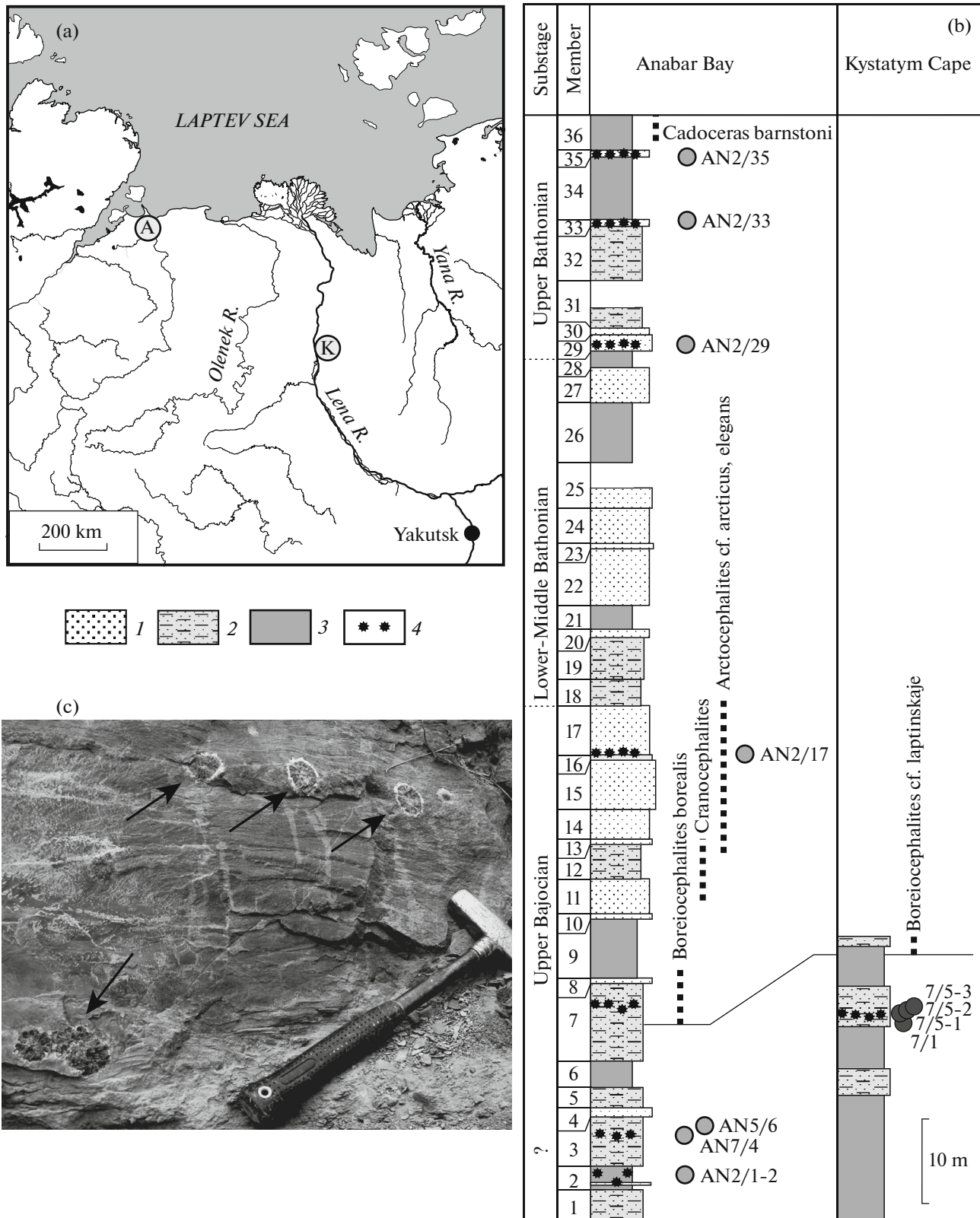


Fig. 1. Location of the sections of the Middle Jurassic (a) and their structure (b) with the position of the selected glendonite samples: (a) the western shore of Anabar Bay, and K, Kystatym Cape. In inset (b), ammonite finds (published data [10, 14]) are shown by dashed lines. In the photo (c) arrows show stellate glendonites. (1) Sandstones; (2) siltstones; (3) clays; (4) glendonites.

Table 1. Trace element contents and Sr isotope values in glendonites from the Middle Jurassic of Northern Siberia and Holocene samples from White Sea

Sample	Stratigraphic position	Mg, %	Mn	Fe	Sr	$^{87}\text{Sr}/^{86}\text{Sr}$
			ppm			
Kystatym Cape						
7/1	Upper Bajocian	0.66	2000	3200	1650	0.70714
7/5-1	Upper Bajocian	0.57	1800	2600	940	0.70707
7/5-2	Upper Bajocian	0.68	1800	5200	965	0.70697
7/5-3	Upper Bajocian	0.58	1430	1600	960	0.70709
Anabar Bay, western shore						
AN2/1-2	Upper Bajocian	0.46	2600	2100	1377	0.70702
AN2/17	Upper Bajocian	0.35	4000	3600	1178	0.70693
AN2/29	Bathonian	0.77	3100	9200	1503	0.70687
AN2/33	Bathonian	0.49	2500	4300	1400	0.70690
AN2/35	Upper Bathonian	0.39	2200	3900	1360	0.70693
Anabar Bay, eastern shore						
AN5/6	Upper Bajocian	0.32	3500	5100	1052	0.70704
AN7/4	Upper Bajocian	0.32	3200	6500	1186	0.70715
White Sea						
I-423-1	Holocene	1.31	220	920	1478	0.70930
I-423-2	Holocene	1.17	620	1700	1447	0.70913

sequent dissolution in 1 N HCl [7, 12]. The Sr isotope composition was measured using a Triton TI multicollector mass spectrometer in the static mode. The resulting discrepancy of $^{87}\text{Sr}/^{86}\text{Sr}$ according to the results of repeated measurements did not exceed 0.000006. All the $^{87}\text{Sr}/^{86}\text{Sr}$ values of the studied samples obtained are normalized to a value in standard SRM-987 = 0.710250 (Table 1).

Compared with modern marine calcareous sediments (Fig. 2), samples of the Holocene glendonites are enriched in Mn (220–620 ppm) and Fe (920–1700 ppm), while the Jurassic glendonites contain even more Mn (1430–4000 ppm) and Fe (1600–9200 ppm). Such high concentrations of Mn and Fe are characteristic of carbonate nodules that crystallize in sandy–clay sediments [13]. However, it is important to note that the Sr concentration in the Holocene and Jurassic glendonites (940–1650 ppm) is comparable to that in the rostra of the Jurassic belemnites and the shells of modern mollusks [5, 7, 12], which is significantly higher than in carbonate nodules (Fig. 2).

Growth of carbonate concretions in sandy–clay sediments usually occurs below the water–sediment boundary in the absence of a geochemical connection with the water environment above. The change in the oxidation–reduction potential in the pore waters of the upper sediment layer is controlled by the activity of bacteria capable of complete removal of dissolved oxygen and decomposition of the organic matter. As a result, a reducing environment is formed in the upper

sediment layer, in which the dissolved Mn and Fe are reduced to Mn^{2+} and Fe^{2+} , which then precipitate in the diagenetic calcite [13]. In this case, depending on the activity of sulfate-reducing or methane-generating bacteria, diagenetic carbonates have a different ratio of Fe/Mn (Fig. 2). However, compared with the sedimentary marine calcites [12], diagenetic carbonates are always enriched in Mn and Fe and depleted in Sr [13]. In the same zone, because of the diagenetic transformation of the sandy–clay sediment, the newly formed carbonates are enriched with radiogenic ^{87}Sr , which is uptaken from clays and feldspars.

The high concentrations of Mn and Fe in the glendonites are fully explained by their crystallization in bottom sediments under the effect of carbon dioxide generated as a result of anaerobic oxidation of methane. However, the Jurassic glendonites are considerably enriched in Sr and have a lower $^{87}\text{Sr}/^{86}\text{Sr}$ than coeval carbonate sediments and diagenetic carbonates. The glendonite samples collected stratigraphically higher in the section yielded the minimal $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 3). It should also be noted that the Sr isotope composition is highly variable in samples from the same stratigraphic level in the Kystatym Cape section. The lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the glendonites cannot be explained by the influence of diagenetic changes in the hosting sandy–clayey sediments, since in this case the pore waters must be enriched in ^{87}Sr .

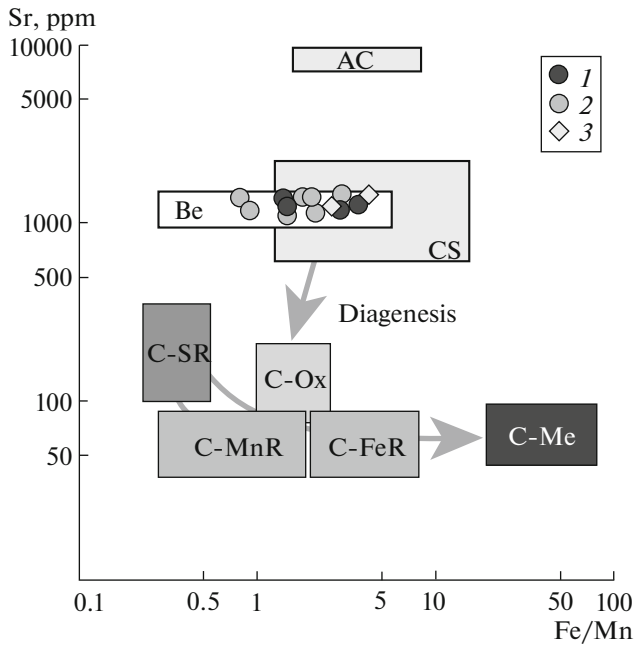
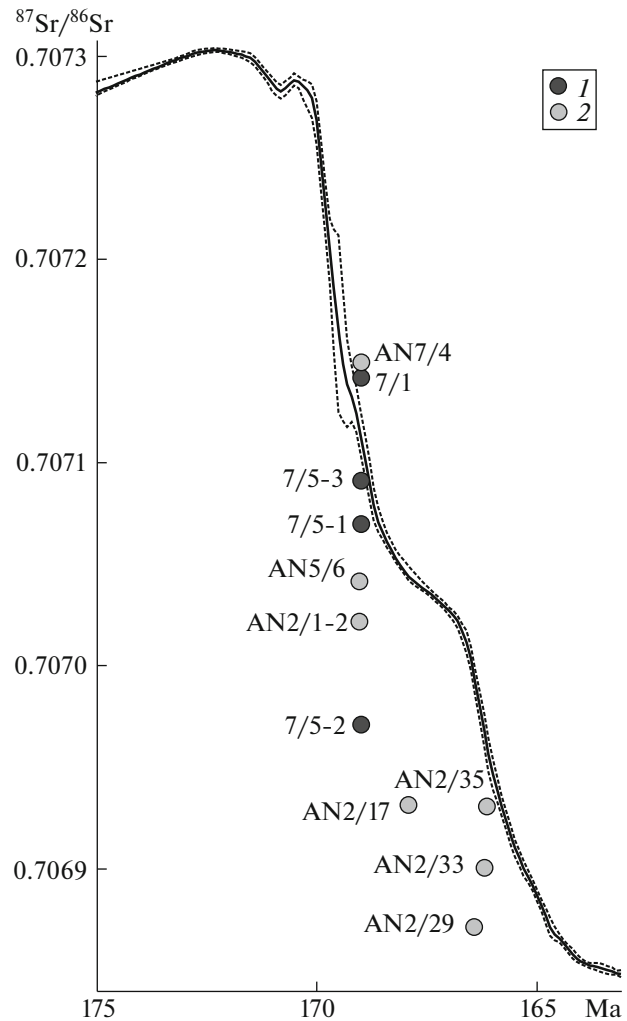


Fig. 2. Sr (ppm) vs Fe/Mn in samples of glendonites, modern carbonate sediments (CS—calcites, AC—aragonites) [12], Jurassic belemnites (Be) [5, 7], and carbonate nodules of various diagenetic zones (C—Ox, oxidation; C—MnR, reduction of Mn; C—FeR, reduction of Fe; C—SR, sulfate reduction; C—Me, methanogenesis) [13]. Samples of Glendonites: (1) Cape Kystatym, (2) Anabar Bay, (3) White Sea.

But there are no volcanogenic minerals and/or tuffs in the Jurassic section.

The reason for the lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the Jurassic glendonites remains unclear. This could be caused by the addition of low-radiogenic Sr together with thermogenic methane of deep origin during the recrystallization of ikaite into calcite. Another reason for the decreased $^{87}\text{Sr}/^{86}\text{Sr}$ in the glendonites of Anabar Bay may be the influence of the younger (Callovian) seawater during the formation of the late calcite generations, although it should be noted that the thickness of the Bathonian interval in the studied sections is 50 to 100 m. The upper layers of the sediment could be imbued with the “younger” seawater, resulting in saturation of the pore waters with strontium with a low $^{87}\text{Sr}/^{86}\text{Sr}$. That was this diagenetic environment in which the later calcite generations depleted in ^{87}Sr could have been formed. This recrystallization processes first of all affected the glendonites in the Upper Bathonian part of the section. The Bajocian glendonites were less affected by diagenetic solutions, and therefore their $^{87}\text{Sr}/^{86}\text{Sr}$ in some samples coincides with this ratio in the late Bajocian seawater (Fig. 3). A similar picture is observed in the Holocene glendonites, in which $^{87}\text{Sr}/^{86}\text{Sr}$ is close to that in the ocean. Thus, the use of glendonites for SIS purposes is possible, but limited by the rate of substitution of ikaite by



Chron of ICS Chart	Opal.	M	B	C	G	P	Z	T	P	H	K	C	L
Substage	Upper	Lower	Mid	Upper	Lower	Upper	Lower	Mid	Upper	Lower	Mid	Upper	
	Aalenian			Bajocian			Bathonian		Callovian				
Series	Lower Jurassic	Middle Jurassic											

Fig. 3. Comparison of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in glendonites with the standard curve of $^{87}\text{Sr}/^{86}\text{Sr}$ variation in the Middle Jurassic Ocean [5]. Samples of glendonites: (1) Cape Kystatym, (2) Anabar Bay.

calcite and the diagenetic history of the sediments under study.

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