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DATA ON $^{87}Sr/^{86}Sr$ RATIO IN REFERENCE SECTION OF THE UPPER KAZANIAN SUBSTAGE

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ABSTRACT
In the present paper $^{87}Sr/^{86}Sr$ ratio values have been presented for the Upper Kazanian regional stratotype section - Pechishchi. The section Pechishchi is unique section formed within the Kazanian palaeosea. The position of received local data on global Phanerozoic evolution $^{87}Sr/^{86}Sr$ curve, in common, is satisfactory. Chemostratigraphic points of the Upper Kazanian substage were determined as $^{87}Sr/^{86}Sr$ values in decreasing trend up the section to the value 0,70727 in top bed 30 dated ~268,5 Ma by the Phanerozoic evolution $^{87}Sr/^{86}Sr$ curve.

Keywords: volga-kama region, the Upper Kazanian substage, ratio $^{87}Sr/^{86}Sr$.

1. INTRODUCTION

The ratio $^{87}Sr/^{86}Sr$ in water of paleobasins is considered as important diagnostic instrument in the understanding of paleobasins evolution [1-3] and in stratigraphic correlation [4-6]. $^{87}Sr/^{86}Sr$ reflects the contribution of strontium by rivers and juvenile matter [7, 8]. Of secondary importance is strontium of groundwater [9], as well as strontium of carbonate diagenetic systems [4, 10, 11]. The isotope composition of the strontium of paleobasins can be traced through the marine carbonate skeletons of shells and carbonate rocks. It can be used as a parameter reflecting the tectonic evolution of the Earth.

The general trend of the $^{87}Sr/^{86}Sr$ variations for the sea water of the Phanerozoic is shown in pioneering works [12-14]. The $^{87}Sr/^{86}Sr$ curve was changed later for some Paleozoic and Mesozoic intervals in [15-17]. A major generalization of the $^{87}Sr/^{86}Sr$ curve for the Phanerozoic was the work [6]. The most recent generalization is the $^{87}Sr/^{86}Sr$ curve for the Phanerozoic was published in [18].

The possibility of dating and correlation of deposits based on a $^{87}Sr/^{86}Sr$ regular variation during geological time. On the one hand, a comparison of the $^{87}Sr/^{86}Sr$ measured values in marine carbonates with the Phanerozoic $^{87}Sr/^{86}Sr$ curve allows one to date the samples under study. On the other hand, the $^{87}Sr/^{86}Sr$ ratio can be used to correlate the sections by comparing $^{87}Sr/^{86}Sr$ values from these sections. The latter task does not require knowledge of the details of the global trend, but it is still necessary to take it into account in order to avoid misunderstandings near the turning points of the trend.

Strontium isotope stratigraphy (SIS) can be used to estimate the duration of geological intervals [19, 20] and for distinguishing between marine and non-marine sedimentation environments [21, 22]. The versatility of $^{87}Sr/^{86}Sr$ is due to the large residence time of strontium in the oceans (about 2 million years) compared with the mixing time of ocean and river water (about 1000 years), and also significant strontium content in seawater (7.6 mg/l) in comparison with river water.

Calibration of the curve $^{87}Sr/^{86}Sr$ [18] is based on biostratigraphic, magnetostratigraphic and astrochronological data (mainly the first two). The difficulties of dating the first two methods are well known. The authors of the $^{87}Sr/^{86}Sr$ curve calibration recognize that the location of the initial ages taken from different sources inevitably contains uncertainties related to interpolation, extrapolation, indirect stratigraphic correlations, and suffers from the ambiguity of stratigraphic boundaries (both biostratigraphic and magnetostratigraphic) and diachronicity. To achieve the most reliable calibration, the statistical nonparametric regression method LOWESS was used. Details of this procedure are described in [23]. However, the authors note that the degree of reliability of the dating of new samples from a given curve depends on the degree of their preservation (in terms of recording the primary signals of the marine environment) and age (the older the age, the greater the uncertainty). The degree of preservation of carbonates is estimated by testing criteria. For example, it has been established that the diagenetic recrystallization of carbonate minerals is characterized by an increase in the content of Mn (and Fe) and a decrease in Sr (and Na) in calcite [10, 11, 24, 25]. Criteria Fe/Sr <5; Mg/Ca <0.024; Mn/Sr <0.2 are the limiting criteria for the degree of diagenesis permissible for isotope comparisons. These criteria are very strict, because they are installed on the shells. When considering carbonate rocks, less stringent criteria are used, for example, Mn/Sr <5; Fe/Sr <20 for limestones and Mn/Sr <20, Fe/Sr <40 for dolomites [24].

It is also important to take into account the ^{87}Rb content in the sample. Upon decay, it becomes ^{87}Sr and is able to influence the $^{87}Sr/^{86}Sr$ ratio. Of course, the Rb^+ ion is so large, and its content in sea water is so small as to worry about its effect on calcite samples, unlike aragonite ones. In general, the content of rubidium should be determined in the samples under study. At concentrations of Rb above 0.1%, corrections in the $^{87}Sr/^{86}Sr$ definitions should be made [5].

This article is devoted to the data on the $^{87}Sr/^{86}Sr$ ratio for Permian paleobasins.

At the end of the Permian period, a global decline in the ocean level and an increase in the area of the continents, a decrease in the basis of erosion led to an increase in the $^{87}Sr/^{86}Sr$ ratio, but before that, the global minimum of this ratio is equal to 0.7069 and is dated as 260 million years ago [18]. The Permian fragment of the global curve is based on two primary sources. The first source is work [16]. The second source is work [26]. These primary sources have significant stratigraphic discrepancies of 3.5 million years by dating, for example, the Permian-Triassic boundary. In addition, the data are mainly based on USA sections. These differences create the above-mentioned uncertainties in the global $^{87}Sr/^{86}Sr$ curve. Therefore, the data from both primary sources are more private than global. Consequently, the binding of new data to the global $^{87}Sr/^{86}Sr$ curve in the Permian interval will obviously be relative and depends on the problems of stratigraphic correlation of new and "reference" measurement points. Whatever it was, today the Permian minimum $^{87}Sr/^{86}Sr$ is attributed to the tops of the Guadelupian division, to the Capitanian formation (in the regional scale of the Volga and the Kama region these deposits are correlated with the Vyatkian horizon) [18]. A small consensus in absolute datings and even in the nomenclature of the Permian is explained by the extremely low sea level and relative faunal poverty in this period. In particular, precipitation at the end of the Permian period was often formed in isolated basins, leading to the dominance of endemic fauna and, as a consequence, to difficulties in inter-basin correlations.

The first data on isotopes of strontium in the marine sediments of Permian Russia are published in [27]. Data were obtained for 25 samples. The data structure basically met the testing Mn/Sr and Fe/Sr criteria. For the early Permian (Asselian and Sakmarian stages), a decrease in the $^{87}Sr/^{86}Sr$ ratio in the range 0.70840-0.70775 was established. For the Kazanian stage, a further drop in the $^{87}Sr/^{86}Sr$ ratio to a local minimum of 0.70725 (the lower part of layer 9 as part of the "layered stone" series) was revealed, and then the ratio was raised to a local maximum of 0.70750 (layer 28 as part of the "sublayer" series). Then the value of this ratio again falls to the value 0.70738 (layer 30 in the series "transitional"), corresponding approximately to the upper boundary of the Kazanian stage.

In present paper new probing data have been presented on unaltered carbonate samples to revise $^{87}Sr/^{86}Sr$ values variation up the section.

2. OBJECT, METHODS AND RESULTS

The object of the investigation was the section of the Upper Kazanian substage of the Pechishchi section the tested layers of the section are described in [28]. The technique for determining the $^{87}Sr/^{86}Sr$ ratio consisted of selection of the least altered samples. The $^{87}Sr/^{86}Sr$ ratio determination was performed in the laboratory of isotope geochemistry and geochronology of IGEM RAS (Moscow). Acids used for the experiments were purified by double distillation without boiling in PFA Teflon apparatus. The water was prepared by the deionization method: preliminary purification was carried out with Elix-3 and the final purification to a resistance of 18.2 MΩ × cm - with Direct-Q (both from Merck Millipore, USA). Chemical preparation was conducted in a dust-free environment of a clean room. Determination of the isotope composition of strontium was carried out in the carbonate fractions isolated by the method introduced by [29]. A sample of 0.01 g of a finely divided probe was dissolved in 10% acetic acid at room temperature. The resulting solution was separated from the insoluble residue in a centrifuge, transferred to a new flask and evaporated to dry salts. The dry residue was dissolved in 6n HCl, the solution was evaporated and the resulting dry residue was dissolved in 2.3n HCl. Strontium for mass spectrometric measurements was isolated using chromatography columns filled with 2.5 ml cation exchanger BioRad AG W50 × 8, in a 2.3N HCl medium. The fractions were evaporated and the dry residue was converted into nitrate. Determination of isotope ratios of Sr was conducted on a thermionic multi-collector mass spectrometer Sector 54 (Micromass, England) using single-tape ion sources made of tantalum tape. The measurements were carried out in a multicolumn dynamic mode [30]. The effect of mass discrimination was taken into account by the normalization method to the isotopic ratio $^{86}Sr/^{88}Sr$ = 0.1194 according to the exponential law. The correctness of the measurements was checked by repeated analyzes of the standard for the isotope composition of strontium NIST SRM-987 with a value of 0.71025.

The results of $^{87}Sr/^{86}Sr$ first and current definitions are presented in Table-1.

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Table-1.

Index	Carbonate rock altered in less extent	$^{87}Sr/^{86}Sr$ data from [27] (normal script), current data (bold black script)
P_2kz_2, bed 30	calcareous-siliceous dolomite	0,70738
P_2kz_2, bed 30	calcareous-siliceous dolomite	0,70737
P_2kz_2, bed 30	calcareous-siliceous dolomite	**0,70727**
P_2kz_2, bed 28	dolomitic limestone	0,70743
P_2kz_2, bed 28	dolomitic limestone	0,70750
P_2kz_2, bed 27	calcareous dolomite	0,70766
P_2kz_2, bed 27	calcareous dolomite	0,70740
P_2kz_2, bed 26	dolomitic limestone	**0,70730**
P_2kz_2, bed 26	calcareous dolomite	0,70745
P_2kz_2, bed 25	calcareous-siliceous dolomite	0,70751
P_2kz_2, bed 24	dolomitic limestone	0,707335
P_2kz_2, bed 22	calcareous dolomite	0,70748
P_2kz_2, bed 21	calcareous dolomite	0,70738
P_2kz_2, bed 21	calcareous dolomite	0,70743
P_2kz_2, bed 21	calcareous dolomite	0,70729
P_2kz_2, bed 20	dolomitic limestone	0,70735
P_2kz_2, bed 19	dolomitic limestone	**0,70732**
P_2kz_2, bed 19	calcareous-siliceous dolomite	0,70726
P_2kz_2, bed 18	dolomitic-siliceous limestone	0,70739
P_2kz_2, bed 17	dolomitic limestone	**0,70731**
P_2kz_2, bed 17	dolomitic limestone	**0,70730**
P_2kz_2, bed 16	calcareous dolomite	0,70734
P_2kz_2, bed 13	calcareous dolomite	0,70729
P_2kz_2, bed 10	calcareous dolomite	**0,70734**
P_2kz_2, bed 9	calcareous dolomite	0,70725
P_2kz_2, bed 9	dolomitic limestone	**0,70730**
P_2kz_2, bed 6,8	magnesian limestone	**0,70740**
P_2kz_2, bed 8	calcareous dolomite	0,70730
P_2kz_2, bed 6	dolomitic limestone	**0,70734**
P_2kz_2, bed 5	dolomitic limestone	0,70749
P_2kz_2, bed 4	magnesian limestone	**0,70735**
P_2kz_2, bed 3	dolomitic limestone	**0,70734**
P_2kz_2, bed 2	dolomitic limestone	**0,70731**
P_2kz_2, bed 1	dolomitic limestone	**0,70732**
P_2kz_1	dolomitic-siliceous limestone	**0,70736**
P_2kz_1	dolomitic limestone	**0,70742**
P_2kz_1	dolomitic limestone	**0,70739**
P_2kz_1	dolomitic limestone	0,70776
P_1s_1	dolomitic limestone	0,70775
P_1a	dolomitic limestone	0,70854
P1a	dolomitic limestone	0,70810
C3	magnesian limestone	0,70815

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3. DISCUSSIONS

The Permian period is characterized by a number of anomalous events. The scale of these events: sea level fall, biological catastrophe and geochemical anomalies are outstanding for the Phanerozoic.

In the Early Permian period, the late Paleozoic ice age, which began in the early Carboniferous, occurs when part of Gondwana was located on the South pole. During the glacial period glaciers covered South America, southern and central

Africa, India, Antarctica and Australia [31]. During the Late Carboniferous, Gondwana migrated to the north, and during the Sakmarian period most of the ice began to melt. The last significant traces of this melting have been found in sediments of the Permian age in Australia and Antarctica, and also in Siberia.

The largest supercontinent in the history of the Earth Pangea was characterized by a sharp continental climate that determined the distribution of climate-sensitive precipitation - coals, aeolian deposits, laterites, reddish sediments and evaporites.

Mass volcanic eruptions of basalts led to the formation of Siberian traps at about the Permian - Triassic boundary. Attempts to date Siberian traps using high-precision techniques point to the Permian-Triassic boundary [32]. It was found in [33] that in the zircon of the boundary layers of the Chinese section, the ^{206}Pb / ^{238}U correlates with the Siberian traps.

The beginning of large-scale basaltic and local silicic eruptions occurs approximately at the end of the cycle of the Earth's magnetic field, known as the super-chrono of Kiama-Illavar. It is noted that the culmination of catastrophic events in the Late Permian and the most intense volcanism occurred several million years after the change of the poles of the Earth's magnetic field [34].

Geochemical anomalies, including dramatic variations of $^{87}Sr/^{86}Sr$ [14, 16] indicate very significant changes in the ocean. The $^{87}Sr/^{86}Sr$ ratio reaches one of the most impressive lows in the history of the Phanerozoic during the Permian period [14, 16]. Changes in $^{87}Sr/^{86}Sr$ before and after the minimum occur at rates comparable to the rate of increase in the values of this ratio over the last 40 million years. According to [32 - 35], the Permian evaporites included about 6% of the strontium reserves from the ocean. However, apparently, this source was of secondary importance in comparison with mantle sources.

The $^{87}Sr/^{86}Sr$ is due to the great influence of tectonic events. Tectonic events in the Permian period connected with the Uralian orogeny. Turning Gondwana clockwise led to the development of collisions in the direction of NE-SW along the Hercinian megasutura, which began to develop in the Late Carboniferous and ended in Early Permian [33 - 36]. The Ural collision between the plates of the Baltic and Kazakhstan also began in the Carboniferous [37, 38]. It was the most intense in Early Permian [37, 39]. Lithological analysis shows that the Ural was high with snow caps in the Sakmarian-Artinskian time. The processes of continental compression have considerably weakened in the Kungurian age. By the end of Permian, the Urals had already become low and considerably eroded [34 - 37]. Thus, the greatest effect of the described orogeny on the $^{87}Sr/^{86}Sr$ indicator in seawater should occur in the Late Carboniferous and Early Permian. With the decline of this influence, the value of juvenile sources increased and the $^{87}Sr/^{86}Sr$ indicator should decrease.

The mechanism of formation of the Permian minimum $^{87}Sr/^{86}Sr$ in the Middle Permian is associated with the increasing importance of climatic processes in comparison with tectonic ones. Pangea was the most soldered and stable at this time. The decrease in $^{87}Sr/^{86}Sr$ was due to a decrease in the melting of ice, sharply continental arid climate, and a small number of watercourses with a huge, high and arid Pangea land [18].

Comparison first $^{87}Sr/^{86}Sr$ data [27] with the $^{87}Sr/^{86}Sr$ ratio with the Phanerozoic $^{87}Sr/^{86}Sr$ curve [6, 18] in the interval 200-350 my concluded that the value of the ratio $^{87}Sr/^{86}Sr$ in a sample of Carboniferous age is 0.70815 and agrees with the curve. Two samples from the Asselian stage from bottom to top have the values $^{87}Sr/^{86}Sr$ 0.70810 and 0.70854. Of these values, only the first agrees with the curve. The second value is greatly overestimated. The sample from the Sakmarian stage has the value $^{87}Sr/^{86}Sr$ 0,70775, corresponding to the Phanerozoic curve in the Artinskian, rather than the Sakmarian stage. The value $^{87}Sr/^{86}Sr$ 0.70776 is determined for the Lower Kazanian limestones (comparable to the Roadian stage of the Guadalupian division), which is much larger than the value of the ratio studied on the curve (approximately 0.70730). The local minimum of 0.70725, which falls on the layer 9, lies about 270 million years (Roadian interval). The local maximum of 0.70749 is higher in the bed 5 [27]. On Figure-1 first data (green colored circles) and current data (red colored circles) for the Upper Kazanian substage are shown in comparison with the Phanerozoic curve. One can see that current data set corresponds to the Phanerozoic curve in more extent than the first data set because of higher sedimentary preservation of newly measured carbonate samples.

Decreasing of $^{87}Sr/^{86}Sr$ values to value 0,70727 was observed up the section to bed 30 (~268,5 Ma). Received data point on choice of “good” samples to reveal strontium isotopes content to characterize the chemostratigraphic points of the Upper Kazanian substage.

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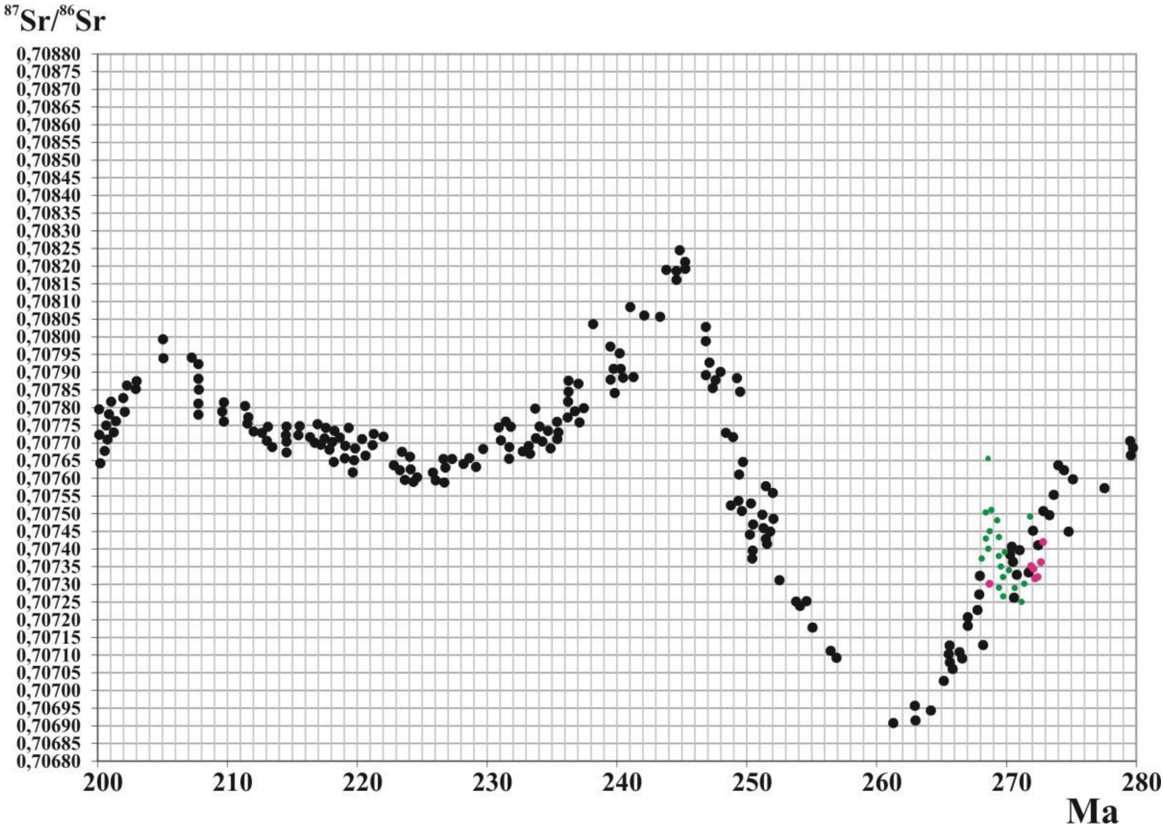

Figure-1. The data sets (red colored circles - current data; green colored circles – data from [27]) on Phanerozoic evolution $^{87}Sr/^{86}Sr$ curve.

4. CONCLUSIONS

Chemostratigraphic points of the Upper Kazanian substage were determined as $^{87}Sr/^{86}Sr$ values in decreasing trend up the section to the value 0,70727 in top bed 30 dated ~268,5 Ma by the Phanerozoic evolution $^{87}Sr/^{86}Sr$ curve.

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