Strontium isotope stratigraphy: Possible applications for age estimation and global correlation of Late Permian carbonates of the Pechishchi type section, Volga River

N. G. Nurgalieva[1], V. A. Ponomarchuk[2], and D. K. Nurgaliev[1]

Received 21 May 2007; revised 30 May 2007; accepted 12 June 2007; published 3 August 2007.

[1] In the present paper the $^{87}Sr/^{86}Sr$ values have been analysed for the Upper Kazanian regional stratotype section – Pechishchi and accompanied sections of Lower Kazanian and also Lower Permian. The section Pechishchi is unique section formed within the Kazanian palaeosea. It is characterized by three Noinsky's cycles of evaporitization of Kazanian palaeosea. The analysis of received data on $^{87}Sr/^{86}Sr$ shows that the highest ratios, characteristic of the Asselian, average at 0.70832. In the Artinskian, the $^{87}Sr/^{86}Sr$ ratios decrease to 0.70774. In the Kazanian, the strontium ratio is much lower: 0.70769 in the Early Kazanian and 0.70740 in the Late Kazanian. The position of received local data on global evolution $^{87}Sr/^{86}Sr$ curve, in common, is satisfactory. The discrepancies between local and global data observed at some points can be explained by the following: local features of the Permian deposition in the eastern part of the Russian Plate (the evaporitic trend and considerable isolation from the ocean); and problems with the chronostratigraphic positioning of the $^{87}Sr/^{86}Sr$ Phanerozoic evolution curve and local $^{87}Sr/^{86}Sr$ curves within the Permian. Multiple determinations of strontium isotope ratios in the Permian carbonates and the isotope dating of key samples would allow the revision of the Permian stratigraphic record. Strontium isotope stratigraphy offers an up-to-date and technologically advanced approach to the stratification and correlation of Permian sedimentary sections on both regional and global scales. *INDEX TERMS:* 0426 Biogeosciences: Biosphere/atmosphere interactions; 1022 Geochemistry: Composition of the hydrosphere; 1041 Geochemistry: Stable isotope geochemistry; 3000 Marine Geology and Geophysics; 9335 Geographic Location: Europe; 9615 Information Related to Geologic Time: Permian; *KEYWORDS:* strontium isotopic stratigraphy, $^{87}Sr/^{86}Sr$ ratio, Permian rocks, carbonates, evaporates.

Citation: Nurgalieva, N. G., V. A. Ponomarchuk, and D. K. Nurgaliev (2007), Strontium isotope stratigraphy: Possible applications for age estimation and global correlation of Late Permian carbonates of the Pechishchi type section, Volga River, *Russ. J. Earth. Sci., 9,* ES1002, doi:10.2205/2007ES000221.

Introduction

[2] The Permian system is a stratigraphically complex formation (particularly, in its upper portion) characterised by numerous regional stratigraphic patterns and, as a result, by ongoing arguments on the international stratigraphic scale. The causes of the existing diversity of viewpoints are well known. During the Permian period, a gigantic continental agglomerate – supercontinent Pangaea-2 – has been formed. By the end of the Permian, the sea level was extremely low. At the end of the Permian period, the greatest biotic termination occurred. Permian sediments accumulated near the land in isolated, endemic, shallow basins with specific faunas. Under the conditions of the global aridisation of the climate and the alternation of marine and continental environments, sediment erosions and depositional breaks became increasingly frequent and the stratigraphic record more complex. It is obvious that the differentiation and correlation of Permian and similar sequences require special tools to identify parameters reflecting the most universal, global changes in the development of the Earth, oceans and seas. Isotope stratigraphy, particularly strontium isotope stratigraphy, is becoming more and more popular as a reliable method to be used for the above purposes.

[3] Strontium isotope stratigraphy is increasingly frequently used for estimating the duration of stratigraphic breaks

[1]Department of Geology, Kazan State University, Kazan, Russia
[2]United Institute of Geology, Geophysics and Mineralogy SB RAS, Novosibirsk, Russia

ISSN: 1681–1208 (online)

and intervals [*McArthur et al.,* 2001) and for identifying marine and non-marine depositional environments [*Poyato-Ariza et al.,* 1998; *Schmitz et al.,* 1991]. The $^{87}Sr/^{86}Sr$ ratio changes regularly over geological time and, therefore, allows age estimation and correlation of sediments. Firstly, the comparison of measured $^{87}Sr/^{86}Sr$ ratios in marine carbonates with the Phanerozoic $^{87}Sr/^{86}Sr$ curve allows time correlation of the studied samples. Secondly, the $^{87}Sr/^{86}Sr$ ratio can be used for correlating sections formed at the same geological time. The latter problem can be solved without possessing detailed data on the strontium ratio's global trend, but this trend should nevertheless be taken into consideration to avoid ambiguities at its turning points.

[4] As a scientific school, strontium isotope stratigraphy was announced in 1948 with a publication [*Wickman,* 1948] showing that the decay of ^{87}Rb and its transformation into ^{87}Sr in the Earth's crust and its further penetration into the hydrosphere govern the strontium isotopic composition over geological time. The $^{87}Sr/^{86}Sr$ ratio was measured in organic carbonates [*Peterman et al.,* 1970] to show that the strontium ratio in seawater decreased during the Palaeozoic, reached a minimum in the Mesozoic and again was increasing up until the present time.

[5] The present strontium content in seawater has been estimated at a sustained level of 7.75 ppm and the isotope ratio at 0.70920. The $^{87}Sr/^{86}Sr$ ratio is governed by the interaction of two major sources of strontium coming into the ocean: weathering zones of silicate minerals producing "river strontium" and hydrothermal sources in the mid-oceanic ridges producing "juvenile strontium" [*Faure,* 1989; *Spooner,* 1976]. River strontium is heavier than juvenile strontium. The mixing of strontium from these two sources forms the final strontium ratio.

[6] The general evolutionary trend of $^{87}Sr/^{86}Sr$ variations in seawater during the Phanerozoic has been demonstrated in the pioneering works on the subject [*Burke et al.,* 1982; *Peterman et al.,* 1970; *Veizer and Compston,* 1974]. The curve published by these authors served as the basis for further studies and conclusions [*McArthur et al.,* 1994; *Veizer et al.,* 1999].

[7] At the end of the Permian period, the global recession of the ocean level, the enlargement of the continent area and the lowering of the base level of erosion increased the $^{87}Sr/^{86}Sr$ ratio, but this phenomenon was preceded by the ratio's global minimum of 0.70685 dated ca. 260 Ma [*Harland et al.,* 1990], i.e. as the Capitanian [*Gradstein et al.,* 2004].

[8] The average rate of the $^{87}Sr/^{86}Sr$ ratio decreased to its minimum during 10 million years was 0.000062 Ma^{-1}, and after passing the minimum it was 0.000097 Ma^{-1}. Model calculations [*Martin and Macdougall,* 1995] showed that these changes were due to varying rates of sediment supply from rivers and juvenile oceanic sources. Weathering in the Late Permian became more intensive in combination with an increase in the content of carbon dioxide.

[9] The $^{87}Sr/^{86}Sr$ decrease at the end of the Sakmarian is associated with a sharply continental arid climate, with a small number of waterways from the vast Pangaean land and, accordingly, with a decrease in the river strontium content [*Harland et al.,* 1990]. A continuous decrease in $^{87}Sr/^{86}Sr$ until the Capitanian with its Permian minimum can be only explained by a more significant phenomenon, such as the activation of light strontium sources. These sources could be represented by Siberian Traps but these are dated as younger rocks: 248±4 Ma by the U/Pb and zircon methods and 249±1.6 Ma by the Ar and biotite methods [*Canaghan et al.,* 1994]. A better explanation is provided by the Eimeshan basalts of Southwest China dated 230–280 Ma, the major portion of which effused during the Late Permian [*Yin et al.,* 1992]. However, the most powerful source could lie in the oceanic spreading zones. Such zones, related to Neotethys, can indeed be modelled [*Korte et al.,* 2006]. The Guadalupian Neotethyan sequences in Oman contain widely occurring pillow lavas overlain by Wordian/Capitanian radiolarites or pelagic limestones [*Bechennec,* 1988; *Pillevuit et al.,* 1997]. Thus, Neotethyan hydrothermal circulation supplied light strontium to the ocean and reduced the $^{87}Sr/^{86}Sr$ ratio. A gradual increase in the $^{87}Sr/^{86}Sr$ ratio during Lopingian time can be explained by the attenuation of basaltic volcanism in Palaeotethys and by an intensified runoff of river water with radiogenic strontium into the ocean. These rivers flowed down from vast continental humid areas. During the Permian, these were mostly in a regressive phase [*Korte et al.,* 2006].

[10] This paper reviews the $^{87}Sr/^{86}Sr$ data acquired from one of the best known Permian open sections, Pechishchi, located on the right bank of the Volga river near the town of Kazan.

Characteristics of the Section

[11] Pechishchi is the Upper Kazanian stratotype that attracted research interest as far back as the late 19th century [*Noinsky,* 1899, 1924]. In general, the Pechishchi section is not confined to a single outcrop. The uppermost layer, described by Noinsky near the settlement of Pechishchi, is Layer 38 of the Podluzhnik member. The upper layers (up to Layer 52) were described by Noinsky near the Truba ravine and correlated with a section near Krasnovidovo. Thus, the Pechishchi section means a composite section of several outcrops.

[12] This research was followed up in detail by other geologists [*Solodukho and Tikhvinskaya,* 1977] who grouped the members identified by Noinsky into four beds (upwards): The Prikazansky strata (Yadreny Kamen and Sloisty Kamen series), the Pechishchi strata (Podboi, Sery Kamen and Shikhany series), the Verkhny Uslon strata (Opoki and Podluzhnik series) and the Morkvashi strata (Perekhodnaya member). The total thickness of the section is 51 m. This paper is based on the published data on the Pechishchi lithostratigraphic section [*Burov and Gubarev,* 1998]. Recent palaeontological and stratigraphic data provide the less detailed stratification of the section into 31 layers instead of the Noinsky's cyclic scheme of 52 layers, although the both patterns are generally in good agreement. This composite section includes Layers 1 to 7 outcropping on the Volga bank

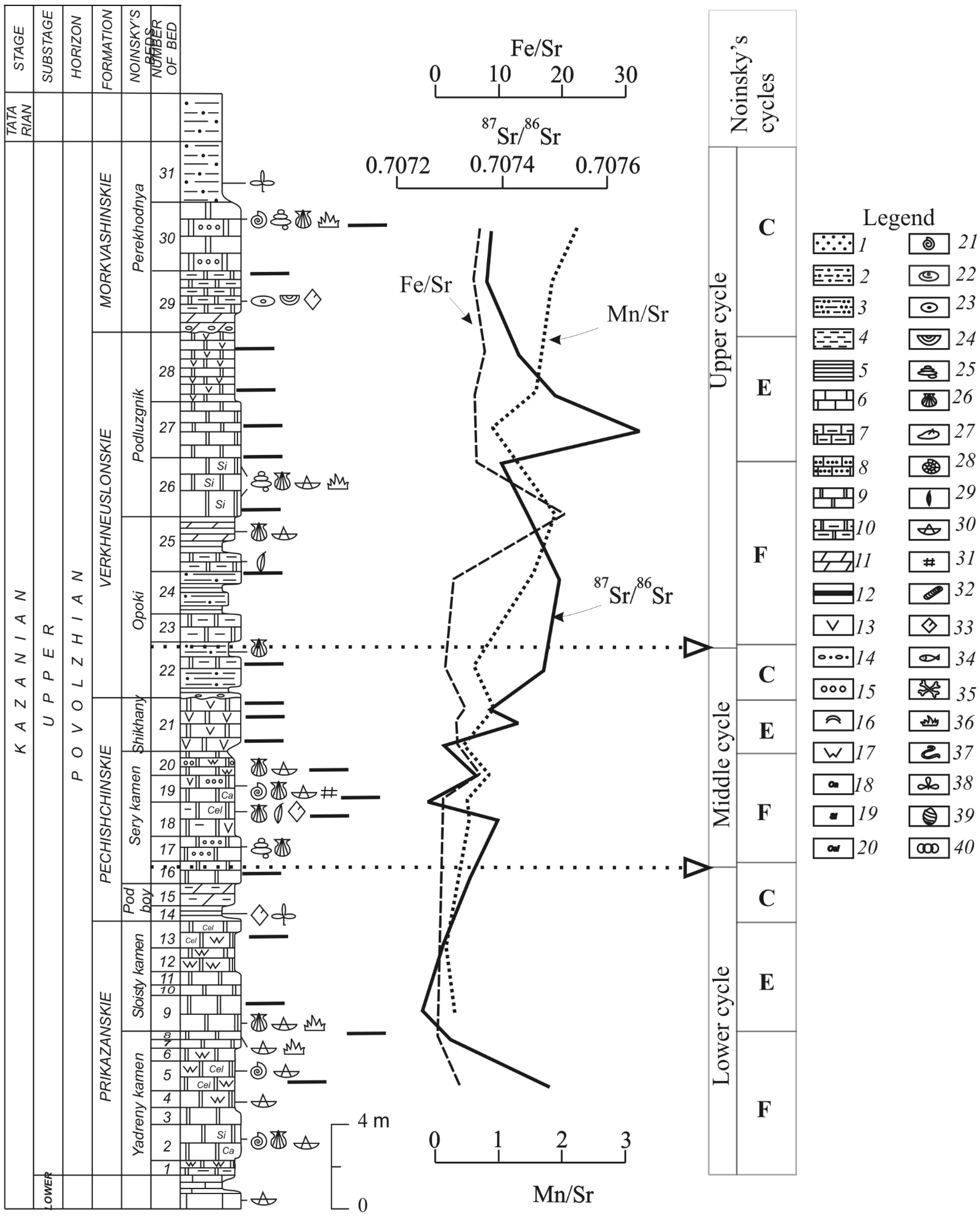

Figure 1. Isotopic-geochemical ratios variations. Pechishchi section. 1 - sandstones, 2 - siltstones, 3 - siltstones and sandstones, 4 - siltstones and clays, 5 - clays, 6 - limestones, 7 - clayer limestones, 8 - sandy limestones, 9 - dolomites, 10 - clayer dolomites, 11 - marls, 12 - coal, 13 - hypsum, 14 - coarse grains, 15 - oolites, 16 - reefs remains, 17 - caverns, 18 - carbonate inclusions, 19 - SiO2, 20 - celestine, 21 - foraminifers, 22 - marine ostracodes, 23 - non-marine ostracodes, 24 - conchostracans, 25 - gastropods, 26 - marine bivalves, 27 - non-marine bivalves, 28 - nautiloidei, 29 - inarticulate brachiopods, 30 - articulate brachiopods, 31 - bryozoans, 32 - crinoids, 33 - fish remains, 34 - finds of fish, 35 - tetrapods, 36 - conodonts, 37 - fauna textures, 38 - plant remains, 39 - charophytes, 40 - miospores. Noinsky's cycles components: F - faunistic carbonate beds, E - evaporites, C -clays and marls.

between Pechishchi and Naberezhnye Morkvashi and Layers 8 to 31 at the bottoms and on the slopes of the Kamenny, Cheremushka and Truba ravines.

[13] Samples for isotope studies were collected from Layers 5, 8, 9, 13, 16, 18, 19, 20, 21, 22, 25, 26, 27, 28 and 30 of the Pechishchi section (Figure 1). The Permian trend was identified and described using core samples of the Lower Kazanian (1 sample), Lower Permian (3 samples) and Upper Carboniferous (1 sample) from Well 1/97 near Naberezhnye Morkvashi representing the Lower Permian continuation of the Pechishchi section. These samples were complemented with one core sample from Well 3 drilled through the Artinskian occurring on the southeastern slope of the South Tatarstan Arch. The samples were collected from the most representative, macroscopically least altered carbonate intervals.

[14] Pechishchi is a unique section that was formed in the Kazanian palaeomarine basin with its axial zone stretching from the lower reaches of the Mezen river through the upper reaches of the Vychegda river, lower reaches of the Kama river and upper reaches of the Sheshma and Sok rivers southwards to Buzuluk. This zone includes the most complete and faunistically richest Kazanian marine sections [*Kotlyar and Stepanov,* 1984]. Shallow-water and coastal deposits containing gypsums and salts occur west and south of the basin's axis (Samarskaya Luka), and the marine, lagoonal and red terrigenous deposits are replaced by the Belebeevo continental formation east of it.

[15] The Pechishchi section clearly features three Noinsky's cycles [*Noinsky,* 1924] associated with the cycles of evaporite formation in the Kazanian palaeosea (Figure 1). Each Noinsky's cycle consists of three components. Lower component – carbonate (rich by marine faunas – on Figure 1 it is signed by letter "F"), middle component – evaporite (carbonates with hypsum and anhydrite – on Figure 1 it is signed by letter "E") and upper component – terrigenous rocks (clays and marls – on Figure 1 it is signed by letter "C"). These components reflect alternation of environments from normal marine ("F") through higher salinity (E) to lake and lagoon conditions ("C").

[16] These cycles are similar to the Zechstein marine cycles identified in Germany and England. In reduced mode, these are also similar to the Lofer cycles in which fauna-rich carbonate beds are replaced by dolomites of tidal and supratidal zones and by red or green clay rocks [*Fischer,* 1964]. Fischer relates changes in the basin depth to eustatic sea-level variations. This interpretation seems to be more credible than the concept suggesting a complex spectrum of local epeirogenic movements of the Earth's crust, although their effect on the sedimentation was not excluded by Fischer. Fischer's calculations suggested that eustatic variations of the sea level could be as high as 15 m and its periodicity could be characterised by a cycle duration varying from 20,000 to 100,000 years.

[17] The origin of the evaporitic component is related to the widely accepted concept that salt basins have to be partially isolated from the open sea by a sill or a bar, supposedly accounting for an increase in water salinity. Otherwise, concentrated brines would flow to the ocean with return currents. Some researchers assume that this isolation could be performed by a physical barrier: for instance, an organic reef, a sand bar or an uplift of sea bedrocks.

[18] The basin model [*Scruton,* 1953] suggests the existence of a dynamic barrier that appeared due to the friction between water masses of different densities, similarly to the pattern observed in the Mississippi river. Such a barrier becomes more effective as the channel, which connects the salt basin with the open sea, shrinks. The barrier should be in dynamic equilibrium affected by such factors as temperature, wind pressure and sea level, each in turn affecting water density in the region.

[19] Some researchers confront the bar hypothesis [*Arkhangelskaya and Grigoriev,* 1960] assuming that water entering a salt basin could already have increased salinity.

[20] Some others also believe that the origin of calcium sulphates and halite does not have to be accounted for by the bar hypothesis as large sand bars could impede water circulation in vast, partly isolated, shallow seas, resulting in the deposition of these evaporites [*Sugden,* 1963]. The above periodicity could, most probably, be controlled by relative changes in sea level and also by the climate. An increase in atmospheric temperature over the whole sedimentation basin enhanced the evaporation that in turn resulted in a higher compensation current from the open sea impeding further increase in salinity. As a result, the evaporitic layer could become thicker. An increase in climatic humidity probably stimulated the entry of fresh waters into the basin by currents from the land reducing the water salinity.

[21] As it appears from the above, strontium ratios from the Pechishchi section can help studying their relation to the open sea and the effect of evaporisation on the sedimentation, allowing at the same time to tie these data to the Phanerozoic strontium ratio curve and to estimate the age of the studied deposits.

Methods

[22] The Rb-Sr classification of carbonates has been studied using the bulk carbonate component after solving a weighed portion of the crushed sample in 10% acetic acid. Rb and Sr have been conventionally separated by the ion-exchange technique using Dowex AG50Wx8 cation exchanger (200 to 400 bags) and 2.5N HCl as an eluent [*Kuznetsov et al.,* 2003]. Rb and Sr contents have been determined by the mass-spectrometric method of isotope dilution using a mixed ^{87}Rb-^{84}Sr indicator. The Sr isotopic composition has been determined by the Finnigan MAT-261 multiple collector mass-spectrometer simultaneously recording ion currents of all isotopes. Isotope studies were conducted at the Institute of Precambrian Geochronology of the Russian Academy of Sciences under the leadership of A. B. Kuznetsov. The ^{87}Sr/^{86}Sr average ratio normalised to ^{86}Sr/^{88}Sr = 0.1194 in the standard SRM 987 sample has been estimated at 0.71025±0.00001.

[23] Carbonates generally have low Rb contents and high Sr contents but can accumulate, over geological spans of time, substantial amounts of radiogenic strontium distorting the determination of the primary isotopic composition.

Table 1. Average isotopic and geochemical characteristics of the composite stratigraphic sequence

Stratigraphy		No of samples	Rb, μg/g	Sr, μg/g	^{87}Rb/^{86}Sr	(^{87}Sr/^{86}Sr)$_0$	Mn, μg/g	Fe, μg/g	Mn/Sr	Fe/Sr
Upper Kazanian (Pechishchi)	Perekhodnaya	2	1.48	180	0.0241	0.70738	324.32	1017.7	2.05	6.44
	Podluzgnik	5	0.39	89	0.0130	0.70749	104.83	667.4	1.44	9.39
	Opoki	2	0.86	264	0.0101	0.70750	396.25	726.5	1.08	2.06
	Shikhany	3	0.75	666	0.0064	0.70737	134.33	732.9	0.69	3.86
	Sery Kamen	4	0.44	229	0.0045	0.70734	106.59	376.4	0.54	2.47
	Sloisty Kamen	2	0.74	349	0.0064	0.70727	89.14	198.1	0.23	0.46
	Yadreny Kamen	2	0.22	1588	0.0016	0.70740	1206.95	769.7	0.04	2.06
Lower Kazanian	Middle Spirifer limestone (Well 1/97)	1	0.68	547	0.0034	0.70769	1624.38	859.6	4.95	2.31
Artinskian		1				0.70774		–		
Well 1/97 column	Sakmarian	1				0.70775	0.70775	587.1	0.08	0.17
	Asselian	2	0.20	140	0.0042	0.70832	0.70831	439.8	1.06	3.23
	Upper Carboniferous	1	0.32	95	0.0099	0.70815	0.70811	197.9	0.14	1.64

[24] The primary strontium isotopic composition of carbonates, corrected for radiogenic strontium, can be calculated using the following formula [*Faure,* 1989]:

$$(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_0 = (^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{meas.}} - {}^{87}\mathrm{Rb}/^{86}\mathrm{Sr}\cdot(e^{\lambda t}-1)\ , \quad (1)$$

where $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{meas.}}$ is the measured Sr ratio in the carbonate specimen, $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_0$ is the primary Sr isotope ratio, $^{87}\mathrm{Rb}/^{86}\mathrm{Sr}$ is the measured ratio of the ^{87}Rb isotope content to the ^{86}Sr isotope content, t is time (years), λ is the ^{87}Rb decay constant of $1.42\cdot10^{-11}$ yr^{-1} [*Neumann and Huster,* 1974].

[25] With t taken as 300 million years, λt of the exponential factor is ca. 10^{-3} and $e^{\lambda t}$ can be expressed as the first two members of the series $1 + \lambda t + (-\lambda t)^2/2! + \dots$. Equation (1) can in this case be expressed as

$$(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_0 = (^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{meas.}} - {}^{87}\mathrm{Rb}/^{86}\mathrm{Sr}\cdot\lambda t\ . \quad (2)$$

[26] The primary Sr isotopic composition can also be distorted due to secondary alterations of carbonates. The degree of preservation/alteration of carbonates has been estimated using published criteria [*Banner and Hanson,* 1990; *Brand and Veizer,* 1981; *Khabarov et al.,* 2000; *Veizer,* 1989].

[27] The separation of samples with disturbed and undisturbed isotopic systems has been performed using the following Mn/Sr and Fe/Sr values: <5 and <20 for limestones and <10 and <60 for dolomites, correspondingly. A differentiated approach to determining the effect of post-sedimentation alterations on primary $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios and carbon and oxygen isotopic compositions is used due to the fact that strontium more easily enters the crystalline lattice of calcite than that of dolomite and, for this reason, strontium concentrations in limestones can be almost ten times higher than in dolomites.

Results

[28] Figure 1 shows the distribution of strontium isotope ratios and Mn/Sr and Fe/Sr ratios for the most representative series of samples from the Upper Kazanian of the Pechishchi section. Table 1 gives average isotopic and geochemical characteristics of the Permian composite stratigraphic sequence.

[29] The general structure of these data satisfies the test criteria Mn/Sr<5 and Fe/Sr<20.

[30] Analysis of the $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_0$ ratios determined for the section shows that the highest ratios, characteristic of the Asselian, average at 0.70832. In the Artinskian, the $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_0$ ratios decrease to 0.70774. In the Kazanian, the strontium ratio is much lower: 0.70769 in the Early Kazanian (Table 1) and 0.70725 to 0.70766 in the Late Kazanian (Figure 1). The Perekhodnaya member is characterised by a ratio of 0.70738 corresponding to the boundary between the Kazanian and Urzhumian dated as ca. 266.8 Ma [*Gradstein et al.,* 2004].

Discussion

Correlation of ^{87}Sr/^{86}Sr Ratios of the Permian From Pechishchi and Associated Sections With the Global Data

[31] Age estimations and correlation of sediments using the $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratio are based on its regular variations over geological time. On the one side, the comparison of measured $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios in marine carbonates with the Phanerozoic

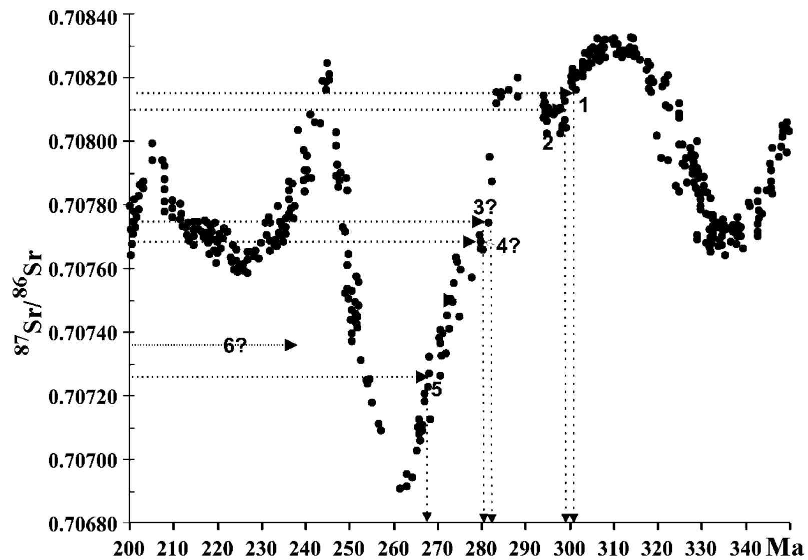

Figure 2. The comparison of the $^{87}Sr/^{86}Sr$ values of local sections data of the Eastern part of Russian plate and $^{87}Sr/^{86}Sr$ Phanerozoic curve [*Gradstein et al.,* 2004; *Veizer et al.,* 1999]. Samples: 1 – upper Carboniferous; 2 – Asselian; 3 – Sakmarian by local definition but Artinskian by global curve; 4 – Lower Kazanian by local definition but Artinskian by global curve; 5 – "Sloisty Kamen" (Upper Kazanian); 6 – "Perekhodnaya" (the end of Kazanian).

$^{87}Sr/^{86}Sr$ curve allows the study of the position of samples relative to this curve. On the other side, the $^{87}Sr/^{86}Sr$ ratio can be used for correlating sections.

[32] Let us correlate the acquired $^{87}Sr/^{86}Sr$ data on the studied section with the Phanerozoic $^{87}Sr/^{86}Sr$ curve for an interval of 200–350 million years (Figure 2). The $^{87}Sr/^{86}Sr$ ratio of 0.70815 in the Carboniferous sample (Point 1 at ca. 301 Ma) is in agreement with the curve. Two Asselian samples (upwards) have $^{87}Sr/^{86}Sr$ ratios of 0.70810 (Point 2 at ca. 299 Ma) and 0.70854. Only the first ratio is in agreement with the curve. The second one substantially deviates upwards. The Sakmarian sample has a strontium ratio of 0.70775 (Point 3 at ca. 279.6 Ma) corresponding to the Artinskian but not to the Sakmarian of the Phanerozoic curve. The Lower Kazanian (or Roadian/Guadalupian) middle Spirifer limestones have a $^{87}Sr/^{86}Sr$ ratio of 0.70769 (Point 4 at ca. 279.5 Ma) corresponding to the Artinskian. The ratio of 0.70727 (Point 5 at ca. 268 Ma), determined for the Sloisty Kamen member, corresponds to the boundary between the Roadian and Wordian. The ratio of ca. 0.70738 (Point 6 at ca. 252 Ma), determined for the Perekhodnaya member, is close to the $^{87}Sr/^{86}Sr$ average ratio of 0.70740. The position of this point on the curve cannot reflect real age corresponding to the end of the Kazanian, probably, due to the dominant effect of the considerable isolation of the local sedimentation basin from the ocean.

[33] The discrepancies observed at some points (Figure 2) can be explained by the following:

[34] 1. local features of the Permian deposition in the eastern part of the Russian Plate (the evaporitic trend and considerable isolation from the ocean),

[35] 2. problems with the chronostratigraphic positioning of the $^{87}Sr/^{86}Sr$ Phanerozoic evolution curve and local $^{87}Sr/^{86}Sr$ curves within the Permian.

[36] The obtained isotope ratios cannot be reliably correlated with the global curve without determining the absolute age of rocks.

[37] Generally, the resulting $^{87}Sr/^{86}Sr$ isotopic ratios from the Permian of the Pechishchi section are well correlated with the global curve. It should also be emphasised that the global curve of $^{87}Sr/^{86}Sr$ variations may contain errors. Some ambiguities relating to the global character of this curve are as follows:

[38] 1. The Permian portion of the curve is controlled stratigraphically without absolute dating.

[39] 2. The character of the curve is in fact not absolutely global. It only contains samples from a number of outcrops, and their age was determined using local stratigraphic scales.

[40] However, general evolutionary features of the Permian palaeobasins are preserved over geological time.

The Nature of $^{87}Sr/^{86}Sr$ Variations in Carbonate Deposits of the Pechishchi Section

[41] It can be assumed that the dispersion of the $^{87}Sr/^{86}Sr$ isotope ratio in the Permian carbonate samples from the Pechishchi section is mostly due to strontium isotope variations that took place in the seawater of the Permian ocean. In some cases, $^{87}Sr/^{86}Sr$ changes can be related to local variations of this ratio in the Permian basins in the eastern portion of the Russian Plate that were separate from the ocean due to the fall of the ocean level. In some samples, $^{87}Sr/^{86}Sr$

changes occur against the background of geochemical variations (Mn/Sr and Fe/Sr deviations in the Asselian, the middle Spirifer limestone and Layer 27 of the Upper Kazanian; see Figure 1) probably caused by the secondary redistribution of strontium and by possible changes in the $^{87}Sr/^{86}Sr$ isotope ratio.

[42] The Early Permian sea basins of the eastern portion of the Russian Plate are characterised by high $^{87}Sr/^{86}Sr$ ratios corresponding to the global $^{87}Sr/^{86}Sr$ ratios in the ocean at that time (Figure 2).

[43] A decrease in the $^{87}Sr/^{86}Sr$ ratio, recorded for the Early Kazanian and early Late Kazanian, generally corresponds to the global curve (Figure 2) and indicates the connection between sedimentation basins and the sea, but local $^{87}Sr/^{86}Sr$ ratios are relatively high reflecting the role of continental water currents that carried heavy strontium. At later times, the salinity of the basin apparently increased, probably due to the aridisation of the climate. Salinisation of the Kazanian palaeobasins over time is indicated by a considerable increase in the content of dolomite (relative to the volume of carbonate rocks), from 40% in the Lower Kazanian to 85% in the Upper Kazanian, and by a two-fold increase in the content of sulphates in the Upper Kazanian relative to the Lower Kazanian [*Sementovsky,* 1973]. The generally low background $^{87}Sr/^{86}Sr$ ratios on the local and global curves indicate the gradual drying of continental currents under arid conditions on the vast Pangaea continent, although their local effect could periodically increase $^{87}Sr/^{86}Sr$ ratios as demonstrated by a local maximum of 0.70766 in Layer 27 (Figure 1).

Conclusions

[44] 1. The strontium isotope ratios recorded in the Pechishchi section clearly indicate the position of the studied Permian deposits on the global curve within the generally accepted time scale. The ambiguities existing at some points are associated with equivocal solutions to chronostratigraphic problems of the Permian system and with the local sedimentation features.

[45] 2. The zonation of $^{87}Sr/^{86}Sr$ isotope ratios corresponds to the stratification pattern. The Lower Permian is characterised by increased strontium ratios and the Kazanian by reduced ones.

[46] 3. The above variations of the isotope ratio are caused by the interaction between land and sea on the one side and between local basins and the ocean on the other.

[47] 4. The obtained isotope data permit the identification of at least three evolutionary types of sedimentation basins in the Volga-Kama region.

[48] Type 1: an Early Permian basin that was apparently a vast, shallow-water, carbonate platform under the active influence of the ocean and climatic changes, such as global glacial processes and local non-glacial evaporation. The $^{87}Sr/^{86}Sr$ ratios are well correlated with the corresponding strontium ratios on the global curve for the ocean and clearly indicate the marine genesis of these deposits.

[49] Type 2: an Early Kazanian basin with $^{87}Sr/^{86}Sr$ ratios generally corresponding to the globally reduced $^{87}Sr/^{86}Sr$ ratios in the oceanic water at that time.

[50] Type 3: a Late Kazanian basin, in which the strontium isotope ratio is expectedly low but higher than on the global curve, which can be explained by the local features of the Upper Permian deposition in the eastern part of the Russian Plate (the evaporitic trend and considerable isolation from the ocean) and by the problems of chronostratigraphic positioning of the Phanerozoic $^{87}Sr/^{86}Sr$ curve and local $^{87}Sr/^{86}Sr$ curves for the Permian.

[51] 5. Multiple determinations of strontium isotope ratios in the Permian carbonates and the absolute dating of key samples would allow the revision of the Permian stratigraphic record. Strontium isotope stratigraphy offers an up-to-date and technologically advanced approach to the stratification and correlation of Permian sedimentary sections on both regional and global scales.

References

Gradstein, F. M., J. G. Ogg, and A. G. Smith, Eds., (2004), *A Geologic Time Scale 2004,* 589 pp., University, Cambridge.

Arkhangelskaya, N. A., and V. N. Grigoriev (1960), Conditions of Formation of Salt Zones in Sea Basins: Lower Cambrian Evaporitic Basin of Siberian Platform, *Izv. Akad. Nauk SSSR, Ser. Geolog.,* No. 4, 41.

Banner, J. L., and G. N. Hanson (1990), Calculation of simultaneous isotopic and trace element variations during water-rock interaction with application to carbonate diagenesis, *Geochim. Cosmochim. Acta, 54,* 3123, doi:10.1016/0016-7037(90)90128-8.

Béchennec, F. (1988), Géologie des nappes d'Hawasina dans les parties orientales et entrales des montagnes d'Oman, *Documents du B.R. G.M., Bureau de Recherches Géologiques et Minières, Orléans, 127,* 1.

Brand, V., and J. Veizer (1981), Chemical diagenesis of a multicomponent carbonate system: 2 Stable isotopes, *J. Sediment. Petrol, 50,* 987.

Burke, W. H., R. E. Denison, E. A. Hetherington, R. Koepnick, H. F. Nelson, and J. B. Otto (1982), Variation of seawater $^{87}Sr/^{86}Sr$ throughout Phanerozoic time, *Geology, 10,* 516.

Burov, B. V., and V. S. Gubarev, Eds., (1998), Upper Permian Stratotypes and Reference Sections in the Prikazansky (Kazan) Region, in *Proceedings of the International Symposium "Upper Permian Stratotypes of the Volga Region",* p. 105, Geos, Moscow.

Canaghan, P. J., S. E. Shaw, and J. J. Veevers (1994), Sedimentary evidence of the Permian/Triassic global crisis induced by the Siberian hotspot, *Can. Soc. Petrol. Geol. Mem., 17,* 785.

Faure, G. (1989), *Principles of Isotope Geology* (in Russian), 590 pp., Mir, Moscow.

Fischer, A. G. (1964),The Lofer cyclothems of the Alpine Triassic, *Kansas. Geol. Surv. Bull., 169*(1), 107.

Harland, W. B., R. L. Armstrong, A. V. Cox, L. E. Craig, A. G. Smith, and D. G. Smith (1990), *A Geologic Time Scale,* 1 pp., University, Cambridge.

Khabarov, E. M., V. A. Ponomarchuk, and I. P. Morozova (2000), *Evolution of Isotopic Compositions of Strontium and Carbon from Carbonates of Riphean Basins on the Western Margin of the Siberian Craton,* 1 pp., OIGGM SO RAN, Novosibirsk.

Korte, C., T. Jasper, H. Kozur, and J. Veizer (2006), $^{87}Sr/^{86}Sr$ record of Permian seawater, *Palaeogeogr. Palaeoclimatol. Palaeoecol., 240,* 89, doi:10.1016/j.palaeo.2006.03.047.

Kuznetsov, A., M. Semikhatov, I. Gorokhov, N. Melnikov,

G. Konstantinova, and E. Kutyavin (2003), Strontium Isotopic Composition of Carbonate Rocks of Karatavian Series of South Urals and Standard Curve of $^{87}Sr/^{86}Sr$ Ratio Variations in Late Riphean Ocean, *Stratigraphy. Geological Correlation, 11*(5), 3.

Kotlyar, G. V., and D. L. Stepanov, Eds., (1984), *Main Stratigraphic Features of the Permian System in USSR,* 280 pp., Nedra, Leningrad.

Martin, E. E., and J. D. Macdougall (1995), Sr and Nd isotopes at the Permian/Triassic boundary: A record of climate change, *Chem. Geol., 125,* 73, doi:10.1016/0009-2541(95)00081-V.

McArthur, J. M., R. Howarth, and T. R. Bailey (2001), Strontium isotope stratigraphy: LOWESS Version 3, Best-fit line to the marine Sr-isotope curve for 0 to 509 Ma and accompanying look-up table for deriving numerical age, *J. Geol., 109,* 155.

McArthur, J. M., W. J. Kennedy, M. Chen, M. F. Thirwall, and A. S. Gale (1994), Strontium isotope stratigraphy for the late Cretaceous: direct numerical age calibration of the Sr-isotope curve for the US Western Interior Seaway, *Palaeogeogr. Palaeoclimatol. Palaeoecol., 108,* 95, doi:10.1016/0031-0182(94)90024-8.

Neumann, W., and E. Huster (1974), The half life of 87Rb measured as difference between the isotopes ^{87}Rb and ^{85}Rb, *Z. Physik, 270,* 121, doi:10.1007/BF01677443.

Noinsky, M. E. (1899), The Permian Section Cropping Out on the Right Bank of the Volga River near Pechishchi Located Opposite the Town of Kazan, *Proceedings of the Kazan Society of Natural Scientists, 13*(6), 34.

Noinsky, M. E. (1924), Some Data on Structure and Facies of the Kazanian in the Prikazansky (Kazan) Region, *Bulletin of the Geological Committee, 13*(6), 565.

Peterman, Z. E., C. E. Hedge, and H. A. Tourelot (1970), Isotopic composition of strontium in seawater throughout Phanerozoic time, *Geochim. Cosmochim. Acta, 34,* 105, doi:10.1016/0016-7037(70)90154-7.

Pillevuit, A., J. Marcoux, G. Stampfli, and A. Baud (1997), The Oman Exotics: a key to the understanding of the Neotethyan geodynamic evolution, *Geodin. Acta, 10,* 209.

Poyato-Ariza, F. J., M. R. Talbot, M. A. Fregenal-Martinez, N. Melendez, and S. Wenz (1998), First isotopic and multidisciplinary evidence for non-marine coelacanth and pycnodontiform fishes: palaeoenvironmental implications, *Palaeogeogr. Palaeoclimatol. Palaeoecol., 144,* 65.

Schmitz, B., G. Aberg, L. Werdelin, S. Bendix-Almgreen, and P. Forey (1991), $^{87}Sr/^{86}Sr$, Na, F, Sr and La in skeletal fish debris as a measure of the paleosalinity of fossil-fish habitats, *Geophysical Society of America Bulletin, 103,* 786, doi:10.1130/0016-7606(1991)103<0786:SSNFSA>2.3.CO;2.

Scruton, P. C. (1953), Deposition of evporites, *Bull. Am. Assoc. Petrol. Geologists, 37,* 2498.

Sementovsky, Y. V. (1973), *Conditions of Formation of Mineral Deposits during the Late Permian in the Eastern Part of the Russian Platform,* 255 pp., Tatknigoizdat, Kazan.

Solodukho, M. G., and E. I. Tikhvinskaya (1977), *Rationale for the Stratification of the Kazanian. Materials on the Upper Permian Stratigraphy in the Territory of the USSR,* 187 pp., University, Kazan.

Spooner, E. T. C. (1976), The strontium isotopic composition of seawater, and seawater oceanic crust interaction, *Earth Planet. Sci. Lett., 31*(167), 74.

Sugden, W. (1963), The hydrology of the Persian Gulf and its significiance in respect to evaporate deposition, *Am. J. Sci., 261,* 741.

Veizer, J., D. Ala, and K. Azmy (1999), $^{87}Sr/^{86}Sr$, $\delta^{13}C$ and $\delta^{18}O$ evolution of Phanerozoic seawater, *Chem. Geol., 161,* 59, doi:10.1016/S0009-2541(99)00081-9.

Veizer, J., and W. Compston (1974), $^{87}Sr/^{86}Sr$ composition of seawater during Phanerozoic, *Geochim. Cosmochim. Acta, 38,* 1461, doi:10.1016/0016-7037(74)90099-4.

Veizer, J. (1989), Strontium isotopes in seawater through time, *Annu. Rev. Earth Planet. Sci., 17,* 141, doi:10.1146/annurev.ea.17.050189.001041.

Wickman, F. E. (1948), Isotope ratios: a clue to the age of certain marine sediments, *J. Geol., 56,* 61.

Yin, Hongfu, Siji Huang, and Kexing Zhang (1992), The effects of volcanism on the Permo-Triassic mass extinction in South China, in *Permo-Triassic events in the Eastern Tethys, World and Regional Geology 2,* p. 146, Cambridge University, Cambridge; New York; Port Chester; Melbourne; Sydney.

D. K. Nurgaliev and N. G. Nurgalieva, Department of Geology, Kazan State University, 18 Kreml. St., Kazan 420008, Russia; E-mail: nouria.nourgalieva@ksu.ru

V. A. Ponomarchuk, United Institute of Geology, Geophysics and Mineralogy SB RAS, 3 Koptyug Pr., Novosibirsk 630090, Russia