

Strontium Isotope Stratigraphy of the Middle–Upper Devonian: Data for the Conodonts from the Central Part of the Volga–Ural Petroleum Province

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This study presents the first $^{87}\text{Sr}/^{86}\text{Sr}$ isotope data for the Middle–Upper Devonian strata of the central part of the Volga–Ural petroleum province, which are based on ramiform conodont elements. The stratigraphic position of most samples was verified using platform conodonts they contained. The $^{87}\text{Sr}/^{86}\text{Sr}$ values obtained are consistent with the global strontium curve, indicating a contiguous connection between this region and the world ocean throughout the Devonian. These results confirm general stratigraphic completeness of the regional succession despite numerous discontinuities and the complex intercalation of black shales, siliciclastics, and carbonates.

Key words: conodonts, Devonian, $^{87}\text{Sr}/^{86}\text{Sr}$ isotope data, Volga–Ural petroleum province

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1 Introduction

The Volga–Ural petroleum province is located on the southeastern margin of the East European Platform, adjacent to the Cis–Ural Foredeep and the Ural Mountains (Fig. 1). The central part of the Volga–Ural province is a large complex multilayer hydrocarbon system confined to the Devonian siliciclastic and carbonate reservoirs (Muslimov, 2007). Owing to its oil-bearing nature, the Devonian stratigraphy of this area has been studied in detail, which makes this region an ideal object for chemostratigraphic studies.

Strontium is one of the most abundant elements in the waters of the world ocean, where its concentration shows low variability and weak dependence on depth and salinity, especially in offshore environment (Lebrato et al., 2020; Castro, Huber, 2003). In the recent ocean, the mean Sr concentration in the water is of $7.85 \pm 0.03 \mu\text{g/g}$ (Brass, Turekian, 1972, 1974). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is determined by two primary sources: the weathering of silicate minerals in terrestrial settings, contributing Sr with a relatively high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, and the hydrothermal activity of mid-ocean

ridges, which produce the Sr with a less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. The contribution of these sources to the total strontium isotopic composition ($^{87}\text{Sr}/^{86}\text{Sr}$ ratio) in seawater can be estimated by the following equation:

$$^{87}\text{Sr}/^{86}\text{Sr}_{sw} = (x)^{87}\text{Sr}/^{86}\text{Sr}_{rw} + (1-x)^{87}\text{Sr}/^{86}\text{Sr}_{hf},$$

where x is the fraction of strontium in seawater derived from river water; and sw , rw , and hf represent the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in seawater (sw), river water (rw), and hydrothermal fluids (hf) respectively.

The possibility of dating and correlating strata using the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is justified by the regular change in this value during geological time. Strontium isomorphically replaces calcium in carbonate, sulphate, and phosphate minerals (including biominerals), but carbonate is the most commonly analysed material due to its widespread occurrence (McArthur, 1994; Veizer et al., 1999).

The determination of Sr isotopes in Palaeozoic strata is complicated by diagenetic alteration of rocks and fossils. Diagenetic alteration of carbonate rocks and fossils can produce changes in the initial Sr isotopic composition in them, creating difficulties for data interpretation. Thus, it is essential to select suitable objects whose stratigraphic resolution matches the Sr residence time in the ocean (approximately 2.4 million years) (Jones, Jenkyns, 2001) and avoid samples with significant post-sedimentation alteration. Signs of alteration include high levels of silicate, and organic matter, and elevated Mn/Sr and Fe/Sr ratios.

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The variation curve of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for Phanerozoic seawater has been established by integrating data from numerous studies, summarised in reviews (McArthur, 1994; Hairuo et al., 1998; Veizer et al., 1999; McArthur et al., 2020). Van Geldern et al. (2006) provided a key study for the Devonian strontium isotope stratigraphy, constructing the most detailed $^{87}\text{Sr}/^{86}\text{Sr}$ curve based on brachiopod shell calcite. Additional reliable data come from studies of brachiopod shell calcite (Brand, 1991, 2004; Zaky et al., 2019) and conodont apatite (Kurschner et al., 1992; Ebner et al., 1997; Veizer et al., 1997; John et al., 2008; Le Houedec et al., 2017; Emsbo et al., 2018). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio shows two maxima, in the Lower Devonian (0.70870) and in the Upper Devonian (0.70808),

separated by a minimum (~ 0.70782) from the base of the Eifelian to the middle Givetian. This well-defined negative excursion, linked to increased hydrothermal activity at mid-ocean ridges or decreased weathering of ^{87}Sr -rich continental rocks (Jones, Jenkyns, 2001), makes $^{87}\text{Sr}/^{86}\text{Sr}$ values suitable for isotope stratigraphy.

Conodonts (class Conodonta, Pander 1856) are extinct small nektonic animals that are similar to the modern chaetognaths. Their tooth-like remains (*conodont elements* or simply *conodonts*), composed of biogenic apatite, are commonly used in strontium isotope stratigraphy (e.g., Kurschner et al., 1992; Ebner et al., 1997; Veizer et al., 1997; Song et al., 2015; Woodard et al., 2013). The strontium

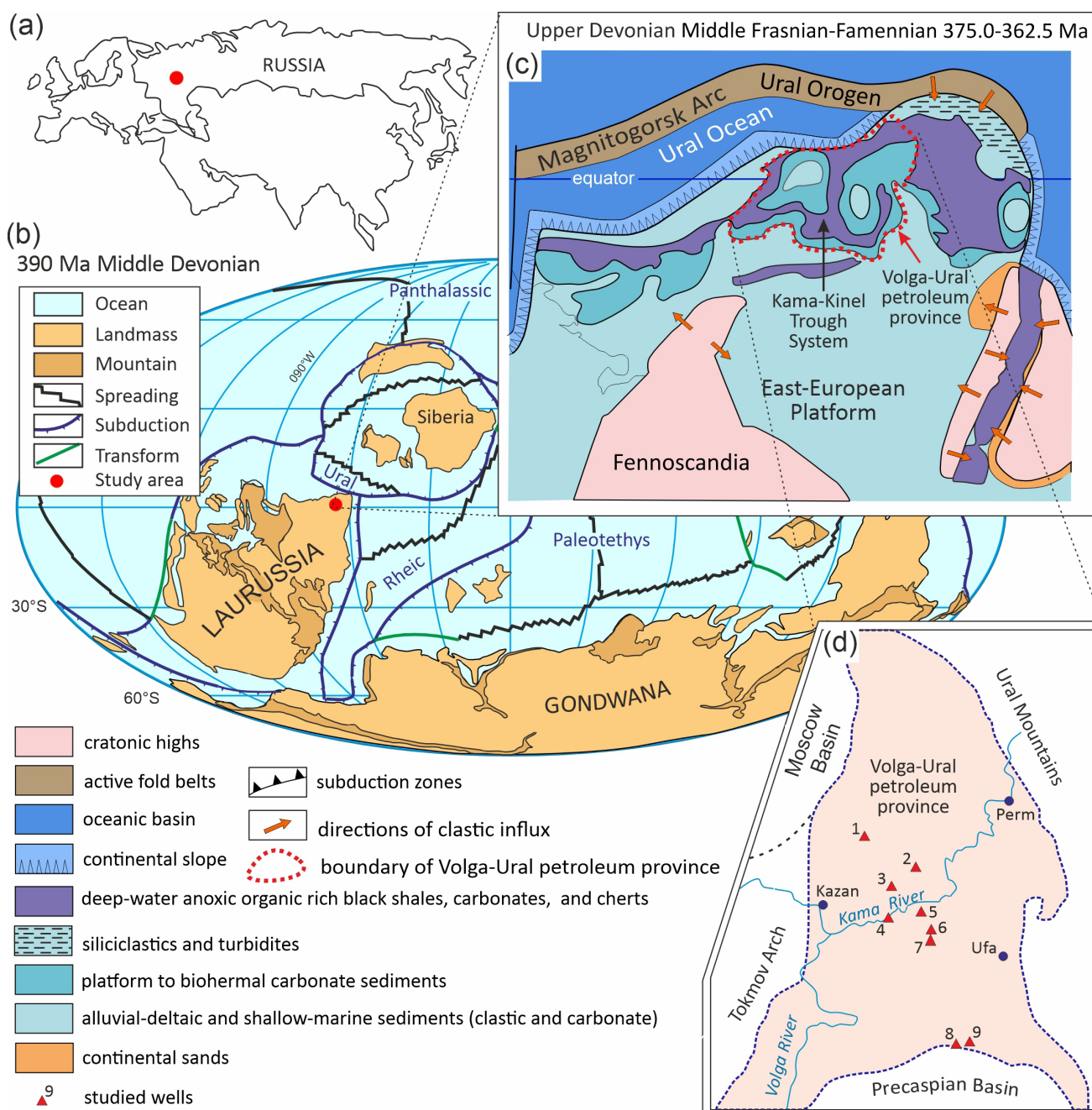


Fig. 1. Location of the studied area and its position in terms of the Middle Devonian palaeogeography: (a) Overview map; (b) Palaeogeographic map (simplified from Golonka (2002), Torsvik, Cocks (2017), Blakey (2021), Scotese (PALEOMAP Project, <http://www.scotese.com/>)); (c) Middle Frasnian to Famennian palaeogeography of the East European Platform and the Ural Palaeo-ocean (simplified from Nikishin et al. (1996), Kabanov et al. (2023a)); (d) location of the studied wells within the Volga–Ural petroleum province

isotopic composition in conodont apatite is thought to reflect the composition of seawater at the time of the existence of these organisms.

Conodonts are characterised by the high content of strontium (0.2 to 0.5 wt%) (Pietzner et al., 1968; Wright, 1989; Wright et al., 1990; Bertram et al., 1992; Katvala, Henderson, 2012), which is incorporated into the bioapatite crystal lattice during the growth of the organism and shows a regular pattern in the conodont hard tissues (Zhuravlev, Shevchuk, 2017). Usually, the maximum amount of strontium is concentrated in paralamellar and albid tissues (“white matter”) (Wright, 1989; Holmden et al., 1996; Zhuravlev, Shevchuk, 2017) of ramiform elements (Holmden et al., 1996), the most common in conodont apparatus. The degree of diagenetic alteration of conodont bioapatite can be assessed by the Colour Alteration Index (CAI), which is used as a proxy of thermal alteration (Kolodny, Epstein, 1976; Epstein et al., 1977). The CAI reflects the alteration and degradation of the organic matter in the conodont tissues. The thermal diagenetic changes in conodont elements also affect the mineral component of the conodont tissues provoking its re-crystallisation and contamination of the conodont bioapatite (Zhuravlev, 2023).

Conodonts offer significant biostratigraphic advantages as objects of chemostratigraphy. Their evolutionary features, ubiquitous distribution in Devonian marine settings, and detailed zonal stratigraphy make them ideal for Sr isotope stratigraphy. The extinction of conodonts in the Late Triassic or earliest Jurassic, which precludes the possibility of direct comparison of their isotope values with modern analogues, is assumed to be the main limitation of conodont application in strontium isotope stratigraphy (Aldridge et al., 1986; Conway-Morris, 1989; Du et al., 2023).

Despite these limitations, the widespread distribution of conodonts in Devonian marine strata, their high strontium content, relative resistance to diagenetic changes, and detailed stratigraphic zonation make conodonts a reliable material for strontium isotope stratigraphy (Kovach, 1980, 1981; Keto, Jacobsen, 1987; Griffin et al., 2021). The aim of this study is the chemostratigraphic interpretation of $^{87}\text{Sr}/^{86}\text{Sr}$ values obtained from the Devonian conodonts of the central part of the Volga–Ural province.

2 Geological settings and palaeogeographic framework

The Devonian of the Volga–Ural petroleum province is represented by the Lower, Middle and Upper Series, with a total thickness of 500–1500 m (Fig. 2). The Lower Devonian is locally distributed, whereas the Middle and Upper Devonian are widespread. The stratigraphic completeness of the Devonian geological record of this area is proved by the contiguous succession of conodont zones (Ziegler, 1962, 1969, 1971; Wittekindt, 1966; Bultynck, 1975; Ziegler, Sandberg, 1984, 1990; Aristov, 1988; Rzhonsnitskaya, Kulikova, 1990; Sandberg, Ziegler, 1996; Ovnatanova, Kononova, 2008; Nazarova, Kononova, 2016, 2020; Fortunatova et al., 2018; Becker et al., 2020), which can be traced from the *kockelianus* Zone of the Eifelian to the Devonian–Carboniferous boundary (Fig. 3).

In the central part of the Volga–Ural petroleum province, the Devonian strata form the basal part of the sedimentary cover and unconformably overlie either the Cryogenian–Ediacaran

rocks in the aulacogens or the crystalline basement. The composition of the strata, faunal assemblages, thickness and completeness of the succession vary considerably over the area. The Devonian strata include black shales, which are considered to be the oil source, and carbonate and siliciclastic rocks serving as reservoirs (Silantiev et al., 2024).

2.1 The Black Shales

They consist of organic rich mixed carbonate-clay or siliceous-clay-carbonate rocks. It is assumed that the organic matter of the black shales has originated under euxinic conditions in the photic zone of the Kama–Kinel Trough System (Fig. 1c) (Kabanov et al., 2023a, 2023b). The thickness of the black shales usually is several hundred metres. The increase in the thickness observed in some cases was probably caused by the growth in the input of siliciclastic material from the adjacent land.

The faunistic assemblages within the black shales exhibit reduced biodiversity of the benthic fauna, including a few species of brachiopods. In contrast, planktonic and nektonic fossils are more diverse and contain radiolarians, ostracods (Entomozoidae), tentaculitids (mainly dacryoconarids), pteropods (winged molluscs), thin-shelled bivalves, cephalopods, etc.

The accumulation of organic-rich black shales began at the end of the Eifelian and continued until the beginning of the Mississippian (Tournaisian). Usually black shales contain conodonts in quantities suitable for isotope analysis.

2.2 Carbonate Sediments

Carbonate sediments were accumulated on isolated carbonate buildups (reefs and banks), and on off-reef carbonate and mud ramps. The isolated carbonate buildups (up to 600 m thick) consist of bioclastic, oolitic, microbial limestones containing a rich assemblage of fossils, including foraminifers, stromatoporoids, corals, brachiopods, crinoids and calcareous algae. Sediments of this type were predominantly accumulated along the slopes of the Kama–Kinel trough system (Fig. 1c). Off-reef carbonate and mud ramps consist of bioturbated limestones and mudstones with diverse benthic assemblages. In some cases, the carbonate successions are characterised by stratigraphic incompleteness and gaps.

During the Late Eifelian to Late Givetian, the accumulation of carbonate sediments was restricted to local troughs and was closely related to the accumulation of black shales. Sustainable accumulation of carbonate sediments began at the Early Frasnian and continued until regional regression in the Early Viséan (Silantiev et al., 2023, 2024). Limestones containing brachiopods and crinoids usually are rich in conodonts; in limestones of other types, conodonts are rare or absent.

2.3 Siliciclastic Sediments

These were accumulated from the late Early Devonian (Emsian) to Early Late Devonian (Frasnian) and, nowadays, are represented by well-sorted sandstones and siltstones interbedded with mudstones. The thicknesses range from hundreds of metres in the troughs to tens of metres in uplifted areas of the tectonic arches. Marine fossils, including conodonts are rare, but various ichnofossil assemblages reveal the marine origin of these sediments (Silantiev et al., 2022, 2024; Miftakhutdinova, 2023).

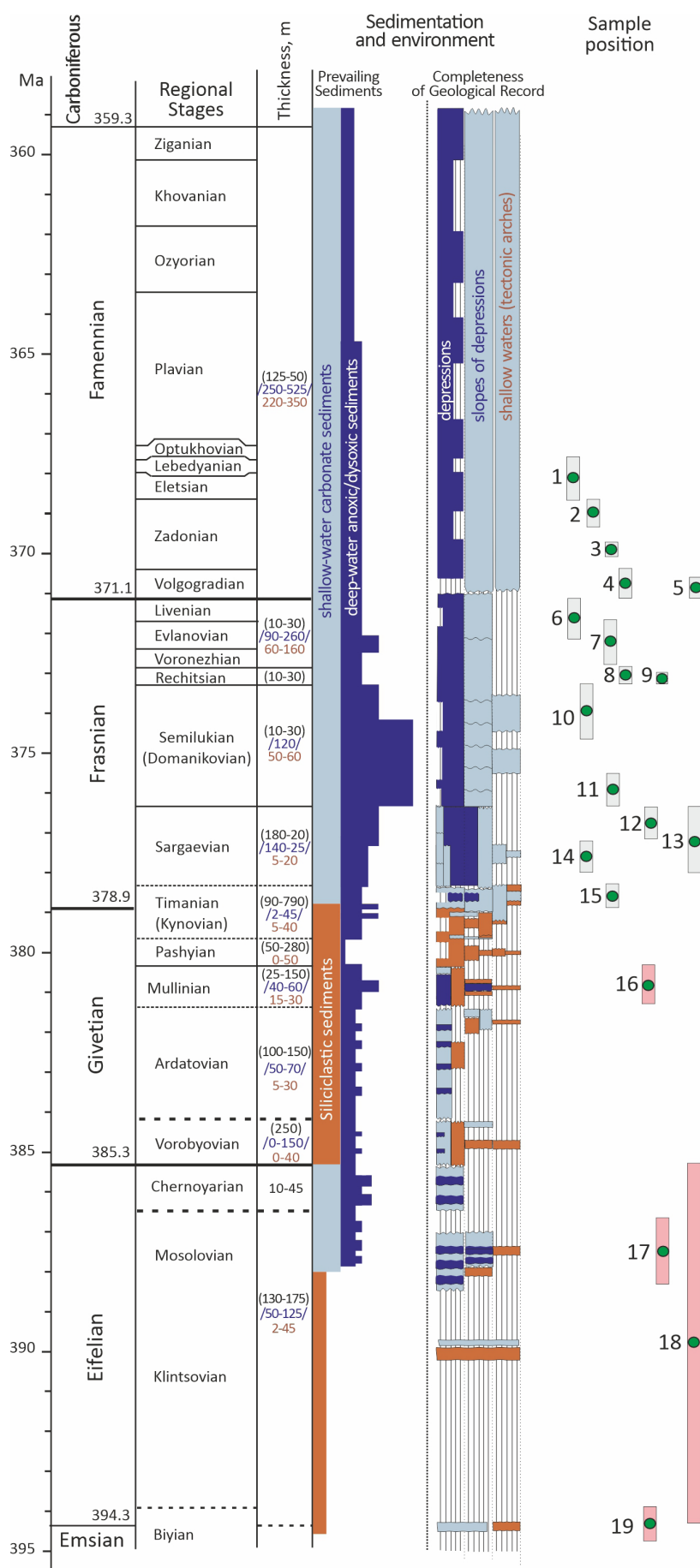


Fig. 2. Main types of sedimentation and completeness of the Devonian succession within Volga–Ural petroleum province. The position of the studied samples is shown. The data on sedimentation are updated from Kabanov et al. (2023a, 2023b). The width of the columns indicates the relative areal distribution of the strata; the white breaks indicate the hiatuses. Thickness indications: black font in parentheses – depressions; blue font in oblique brackets – slopes of depressions; brown font – shallow waters (modified from Silantiev et al. (2024)).

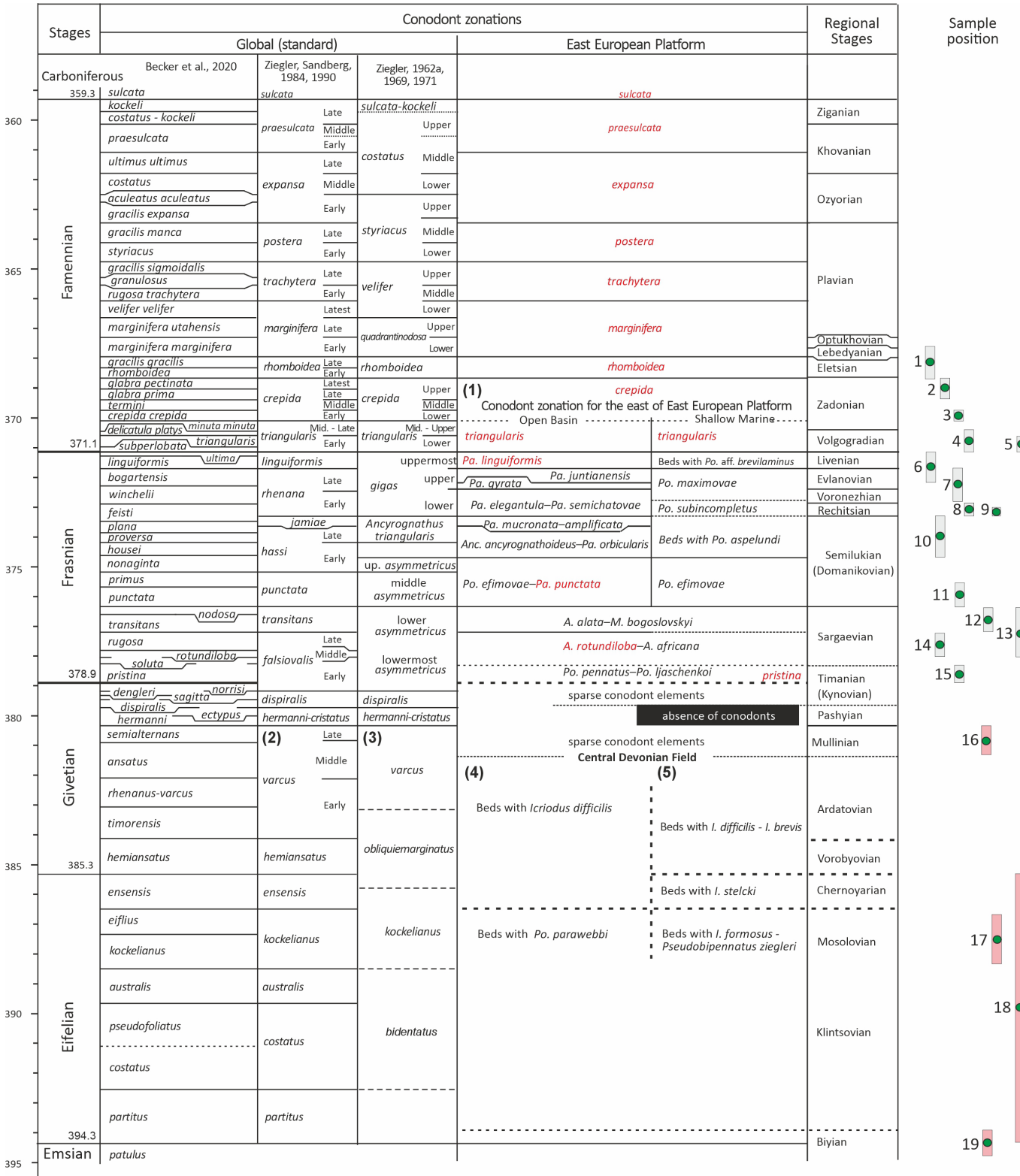


Fig. 3. Position of the studied samples within the framework of the Middle and Late Devonian conodont zonations and regional stratigraphy. Conodont zonations are compiled from: (1) Ovnanova, Kononova (2008); (2) Sandberg, Ziegler (1996); (3) Bultynck (1975), Aristov (1988); (4) Aristov (1988); (5) Nazarova, Kononova (2016, 2020); red font indicates global or standard conodont zones traceable in the Volga–Ural petroleum province. Regional Stages are given according to Rzhonsnitskaya, Kulikova (1990) and Fortunatova et al. (2018). Samples: the grey rectangles indicate the age determined on conodont data; pink rectangles mean that the position of the sample is determined on geological data; scheme of conodont zonations is modified from Silantiev et al. (2024).

3 Materials and Methods

Conodont elements for $^{87}\text{Sr}/^{86}\text{Sr}$ analysis were selected from the extensive collection of the Geological Museum of the Kazan Federal University (coll. nos. 34/24, 34/93, 34/97, 34/99, 34/100), originally assembled by Professor Vyacheslav G. Khalymbadza (Khalymbadza, 1981, 2011). In the 1960–1980s, this collection was used to determine the conodont zonation of the Volga–Ural petroleum province (Khalymbadza, Chernysheva, 1969a, 1969b, 1970a, 1970b). A total of 19 samples from different stratigraphic levels were analysed (Fig. 2, 3).

For $^{87}\text{Sr}/^{86}\text{Sr}$ analysis, we used conodonts from carbonate rocks of different facies composition, both from anoxic black shales and from shallow oxic carbonate strata. Such multifacial sampling should not have affected the $^{87}\text{Sr}/^{86}\text{Sr}$ values, because the concentration of strontium in seawater is determined by its residence time and is practically independent of basin depth and oxic or anoxic environment, i.e. it is determined only by the rate of strontium input (e.g. from river water or hydrothermal vents) and removal from water (e.g. by precipitation in minerals or participation in biological processes).

The exact stratigraphic position of samples within the conodont zonation and regional stages was determined using platform conodonts where available (Supplementary Material: Figures S1–S5). This approach enabled accurate correlation of most samples with the International Chronostratigraphic Chart (Fig. 3). However, four samples (16–19) lacked platform conodonts and their stratigraphic positions were inferred from geological data, leading to greater uncertainty (Fig. 2).

The $^{87}\text{Sr}/^{86}\text{Sr}$ values were measured predominantly from ramiform elements, which are characterised by a higher strontium content (Holmden et al., 1996). In addition, ramiform elements have a smoother surface than platform conodonts, reducing the retention of extraneous mineral particles. Conodont elements were extracted from the host carbonates with acetic acid and were selected manually under a binocular microscope and cleaned of extraneous mineral particles where necessary. The selection process took into account the Conodont Colour Alteration Index (CAI) and the state of preservation of the conodonts. Only specimens with a CAI of 2 or less and showing no signs of redeposition, such as surface erosion or rounding, were selected.

The isotopic composition of Sr in conodonts was studied using thermal ionisation mass spectrometry. The sample weight did not exceed ~0.015 g. The chemical preparation was reduced to dissolution of the sample in 6 M HCl at atmospheric pressure and a temperature of 110 °C for 10–12 hours. The resulting solutions were centrifuged and evaporated. Pure fractions of Sr for mass spectrometric analysis were obtained by ion exchange chromatography. The separation of Sr from matrix elements was carried out in 2.4 M HCl medium on ion-exchange columns filled with 3 mL of Bio Rad W50x8 resin (200–400 mesh). The procedural blanks contained less than 0.1 ng of Sr. The Sr isotopic composition was analysed on a Sector 54 Multicollector Thermionisation Mass Spectrometer (Micromass, UK). Measurements were performed on oxidised tantalum in single-filament mode with a current of centre filament of 2.2–2.7 A, corresponding to a temperature range

of 1380–1450 °C. The measurement experiment included the registration of 100 mass-spectra, which provided convergence of results within the analysis no worse than 0.002% (2SE). The accuracy of the mass spectrometric measurements of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the samples was controlled by systematic measurements of the international standard of Sr isotopic composition (SRM-987, NIST, USA). Over the period of analysis, the value of $^{87}\text{Sr}/^{86}\text{Sr}$ for the SRM-987 standard was 0.710246 ± 0.000016 ($n = 10$, 2SD).

In addition to the standard control, the accuracy of the $^{87}\text{Sr}/^{86}\text{Sr}$ values was checked on a sample from the lower Kungurian (Cisuralian) of the Mechetlino reference section. The $^{206}\text{Pb}/^{238}\text{U}$ age of 283.5 ± 0.6 Ma for this sample (Supplementary Material, Table S1, Fig. S3.9) was estimated with high accuracy using a combination of biostratigraphic and radioisotope geochronological methods (Schmitz, Davydov, 2012). The $^{87}\text{Sr}/^{86}\text{Sr}$ value of this sample is 0.707394 ± 0.000010 and fits well with the global strontium curve for the Early Kungurian.

The $^{87}\text{Sr}/^{86}\text{Sr}$ data were used to compute a *Loess* model similar to that used by McArthur et al. (2001), with the smoothing algorithm developed by Cleveland (1979) and Cleveland and Devlin (1988). The *Loess* algorithm employs local regression, a statistical method for fitting smoothing curves without prior assumptions about their shape. The curve was generated using R, an open-source statistical software environment (R Core Team. A language and environment for statistical computing. R Foundation for Statistical Computing, <https://www.R-project.org/>).

4 Results and Discussion

The $^{87}\text{Sr}/^{86}\text{Sr}$ values of the Devonian conodonts from the central part of the Volga–Ural petroleum province, along with the *Loess* trend line, are presented in Figure 4 and in Supplement, Table S1. Sample 19 (Lower Devonian, Biyan regional stage) shows an outlier value, probably due to diagenetic alteration of the conodont material, and is excluded from further discussion. We compare our results with the global Devonian strontium curve derived from brachiopods (Van Geldern et al., 2006) and referenced in the recent Geologic Time Scale volume (McArthur et al., 2020). The overall $^{87}\text{Sr}/^{86}\text{Sr}$ values range from 0.707780 ± 0.000012 to 0.708238 ± 0.000018 , which are broadly in line with the global trend.

The data clearly reveal two distinct groups of samples, with the first group showing average $^{87}\text{Sr}/^{86}\text{Sr}$ values between 0.7077 and 0.7079, and the second group having values in the range of 0.7081 to 0.7082. The lower $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.707780–0.707960) are characteristic of the Middle Devonian and Early Frasnian conodonts, whereas the higher values (0.708103–0.708238) are associated with the late Frasnian and Famennian conodonts. The reduced $^{87}\text{Sr}/^{86}\text{Sr}$ values in the middle and upper Eifelian can be attributed to increased input of Sr from mantle sources into the world ocean and/or reduced weathering of ^{87}Sr -rich crustal rocks (McArthur et al., 2020).

During the Givetian, a gradual increase in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is observed. This positive shift, more clearly recorded in the upper Givetian, is generally consistent with the brachiopod-derived strontium curve (Van Geldern et al., 2006).

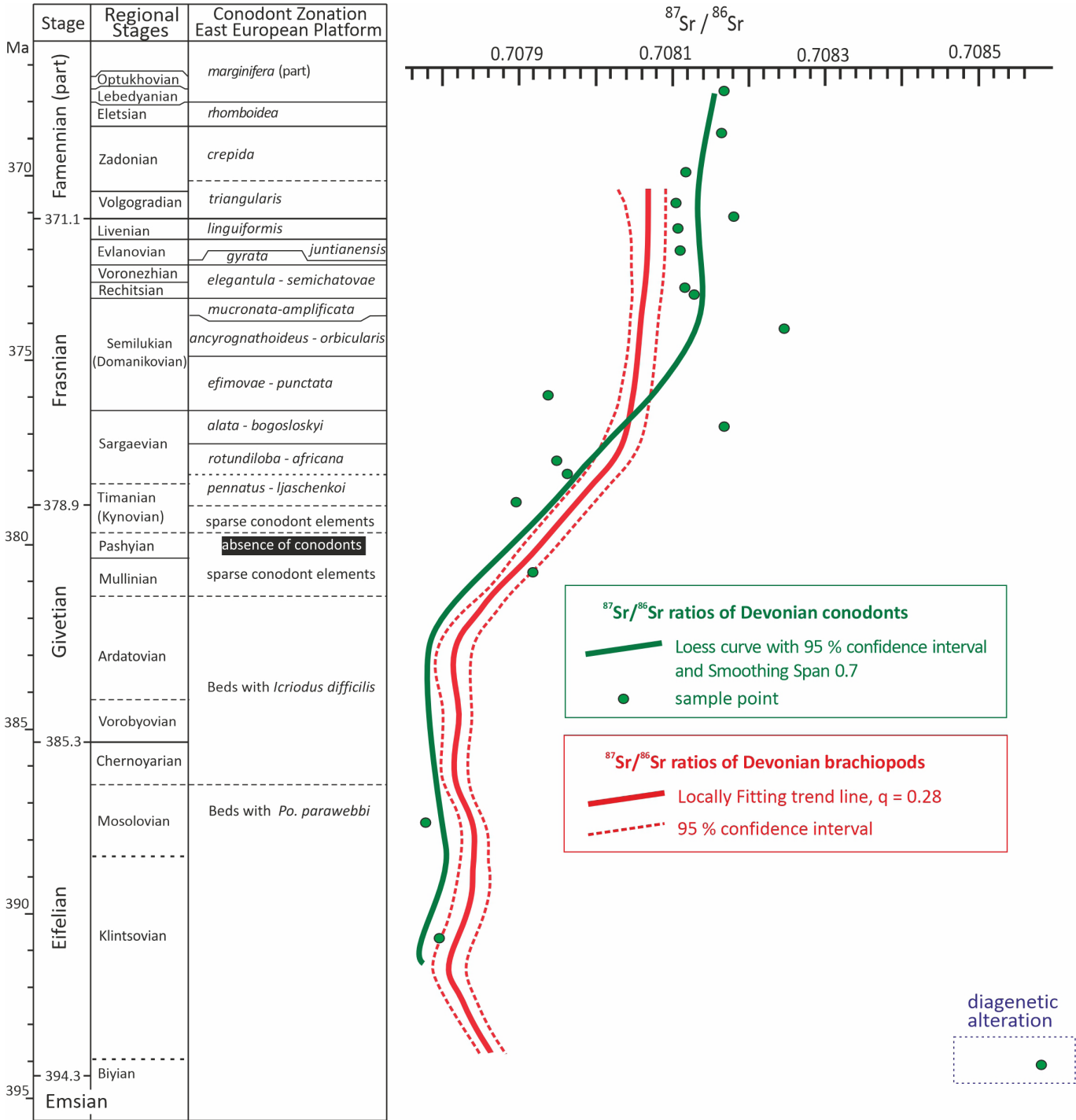


Fig. 4. $^{87}\text{Sr}/^{86}\text{Sr}$ values and Loess trend line for Devonian conodonts from the central part of the Volga–Ural petroleum province compared with the strontium curve for brachiopods (Van Geldern et al., 2006)

The positive $^{87}\text{Sr}/^{86}\text{Sr}$ excursion in the middle to late Givetian can be interpreted as a consequence of the Acadian–Eovariscan orogeny, expanding the global area of rock weathering and increasing the release of ^{87}Sr from crustal rocks into the world ocean (Van Geldern et al., 2006).

The $^{87}\text{Sr}/^{86}\text{Sr}$ values continue to rise in the Early Frasnian, reaching higher levels during the late Frasnian and Early Famennian. The plateaus of elevated values in this stratigraphic interval generally correspond well with the trend observed in the brachiopod-derived strontium curve (Van Geldern et al., 2006). However, the conodont-derived strontium curve shows slightly higher values than the brachiopod-derived curve, a pattern also noted by other researchers (e.g. Ebner et al., 1997; Zaky et al., 2019).

The global $^{87}\text{Sr}/^{86}\text{Sr}$ curve for the Middle–Upper Devonian is mainly based on data obtained from brachiopod shells (Van Geldern et al., 2006; McArthur et al., 2020, and others), although the Sr isotopic composition of Devonian conodonts has also been extensively studied (e.g., John et al., 2008; Woodard et al., 2013; Song et al., 2015; Le Houedec et al., 2017; Emsbo et al., 2018). Conodont elements exhibit relatively high chemical stability and low permeability of hard tissues which lack open pores. During biomineralisation, strontium is gradually incorporated into conodont bioapatite, resulting in a regular distribution of Sr within the hard tissues (Zhuravlev, Schevchuk, 2017). The Sr concentrations in the lamellar and paralamellar tissues of conodont elements show oscillations correlated with the periodic growth of the lamellae (Zhuravlev, Shevchuk, 2017; Shirley et al., 2018). The average Sr concentration in conodont element depends on its growth rate, stage of ontogeny, and, probably, taxonomy (Shirley et al., 2018). Despite the complex Sr distribution pattern in conodont elements the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios clearly show very little variation both within a sample and a conodont element. Thus, it is supposed that Sr-isotope signal in conodont elements is independent from conodont taxonomy and the stage of ontogeny, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in conodont elements directly reflect those in the ancient sea water (Bertram et al., 1992; Terrill et al., 2022). There is no clear evidence of diagenetic exchange of Sr between well-preserved conodont elements and the host rock or pore water (Zhuravlev, Schevchuk, 2019). However, conodonts can absorb manganese (Mn) and rare earth elements (REE) from clayey host rocks (Bertram et al., 1992; Bright et al., 2009; Trotter et al., 2016; Zhuravlev, 2023).

Several recent publications have examined the differences in the Sr isotopic compositions of conodonts and brachiopods (Zaky et al., 2019; Woodard et al., 2013; Song et al., 2015). Specifically, conodonts from the Bird Spring Formation (Carboniferous) have higher levels of the radiogenic isotope ^{87}Sr than brachiopods do (Zaky et al., 2019). The authors suggest that this discrepancy may result from diagenetic alterations in the Sr isotopic composition of conodonts. However, such variations could also be caused by regional or local factors. In particular, this assumption is supported by the Permian–Triassic Sr isotope record of conodonts and brachiopods, where the Sr isotope values are in good agreement (Song et al., 2015).

The $^{87}\text{Sr}/^{86}\text{Sr}$ values obtained for the conodonts from the central part of the Volga–Ural petroleum province are largely consistent with those of Devonian brachiopods which are incorporated into the global curve (Fig. 4). However, in some

conodont samples, the $^{87}\text{Sr}/^{86}\text{Sr}$ values show slight deviations. It is unlikely that only diagenetic processes affecting the conodont elements can explain all these discrepancies.

The lower $^{87}\text{Sr}/^{86}\text{Sr}$ values in the Mosolian (Eifelian) and late Timanian–Sargaevian (Early Frasnian) could have been caused by the extensive transgression as well as volcanic and hydrothermal activity in the Ural palaeocean, which was connected with the Kama–Kinel trough system. In contrast, the higher $^{87}\text{Sr}/^{86}\text{Sr}$ values in the Late Frasnian–Famennian could correspond to the enhanced weathering of the western part of the East European Platform.

Our results demonstrate that the general trend of the Devonian $^{87}\text{Sr}/^{86}\text{Sr}$ curve for conodonts from the central part of the Volga–Ural petroleum province aligns with the trends of strontium curves for brachiopods, carbonate rocks, and conodonts from other regions (Ebner et al., 1997; Diener et al., 1996) and with the global $^{87}\text{Sr}/^{86}\text{Sr}$ curve (Van Geldern et al., 2006; McArthur et al., 2020) complementing these data with regional variations.

Conclusion

1. The $^{87}\text{Sr}/^{86}\text{Sr}$ curve for the conodonts from the central part of the Volga–Ural petroleum province aligns with the global strontium curve, indicating a connection between this region and the global ocean throughout the Devonian.
2. The lower $^{87}\text{Sr}/^{86}\text{Sr}$ values in the Eifelian and Early Frasnian could have been caused by the extensive transgression as well as volcanic and hydrothermal activity in the Ural palaeocean, which was connected with the Kama–Kinel trough system. In contrast, the higher $^{87}\text{Sr}/^{86}\text{Sr}$ values in the Late Frasnian–Famennian could correspond to the enhanced weathering of the western part of the East European Platform.
3. Future research could focus on investigating the causes of discrepancies in Sr isotope values between brachiopods and conodonts.

Supplementary Materials

Table S1: $^{87}\text{Sr}/^{86}\text{Sr}$ values, stratigraphy of the samples and conodont assemblages using for age determination

Figures S1–S5: Conodont assemblages used for determining the stratigraphic age of the samples

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Supplementary Material

Table S1

⁸⁷Sr/⁸⁶Sr values, stratigraphy of the samples and conodont assemblages using for age determination

Sample, no.	Well, no.	Stratigraphy	Conodont assemblages	⁸⁷ Sr/ ⁸⁶ Sr ±2σ
1	7	Eletsian–Lebedyanian, <i>rhomboidea</i> Zone – <i>marginifera</i> Zones	<i>Palmatolepis minuta subtilis</i> , <i>Palmatolepis minuta minuta</i> , <i>Pa. glabra glabra</i> , <i>Pa. lobicornis</i> (Fig. S1: 1–7)	0.708162±0.000010
2	2	upper Zadonian, <i>crepida</i> Zone (upper part)	<i>Palmatolepis minuta subtilis</i> , <i>Pa. glabra glabra</i> , <i>Pa. minuta minuta</i> , <i>Pa. superlobata superlobata</i> , <i>Pa. marginifera</i> , <i>Polygnathus nodocostata nodocostata</i> (Fig. S1: 8–10)	0.708158±0.000010
3	7	Zadonian, <i>crepida</i> Zone (lower part)	<i>Palmatolepis</i> sp. (Fig. S1: 11)	0.708113±0.000008
4	2	Volgogradian, <i>triangularis</i> Zone	<i>Palmatolepis tenuipunctata</i> , <i>Pa. minuta</i> , <i>Pa. regularis</i> , <i>Pa. superlobata superlobata</i> (Fig. S1: 12–16)	~0.7081
5	2	lower Volgogradian, <i>triangularis</i> Zone	<i>Palmatolepis triangularis</i> , <i>Pa. superlobata superlobata</i> , <i>Pa. minuta</i> (Fig. S2: 1–3)	0.708174±0.000020
6	8	Evlanovian–Livenian, <i>juntianensis</i> Zone – <i>linguiformis</i> Zone	<i>Polygnathus aspelundi</i> , <i>Po. cf. costulatus</i> , <i>Po. komi</i> , <i>Po. cf. krestovnikovi</i> , <i>Po. lodinensis</i> , <i>Po. pennatus</i> , <i>Po. politus</i> , <i>Po. webbi</i> (Fig. S5: 1–10)	0.708103±0.000010
7	1	Voronezhian–Evlanovian, <i>elegantula-semichatovae</i> Zone – <i>juntianensis</i> Zone	<i>Ancyrodella nodosa</i> , <i>An. ioides</i> , <i>Pa. sp.</i> (Fig. S2: 4–5)	0.708106±0.000007
8	4	lower Rechitsian, <i>elegantula-semichatovae</i> Zone	<i>Palmatolepis hassi</i> , <i>Pa. gigas gigas</i> , <i>Pa. aff. gyratus</i> , <i>Pa. jamieae</i> , <i>Pa. nasuta</i> , <i>Pa. plana</i> , <i>Polygnathus</i> sp. (Fig. S3: 1–8)	0.708124±0.000017
9	2	lower Rechitsian, <i>elegantula-semichatovae</i> Zone	<i>Polygnathus</i> sp., <i>Po. ljaschenkoae</i> , <i>Palmatolepis</i> aff. <i>kireevae</i> (Fig. S2: 6–7)	0.708104±0.000010
10	4	upper Semilukian, <i>An. ancyrognathoides</i> – <i>Pa. orbicularis</i> Zone – <i>Pa. mucronata-amplificata</i> Zone	<i>Palmatolepis proversa</i> , <i>Pa. cf. punctate</i> , <i>Pa. aff. subrecta</i> , <i>Ancyrodella nodosa</i> (Fig. S2: 8–11)	0.708238±0.000018

11	6	lower Semilukian, <i>Po. efimovae</i> – <i>Pa. punctate</i> Zone (lower part)	<i>Polygnathus</i> aff. <i>grandidentatus</i> , <i>Po. lingulatus</i> (Fig. S2: 12–13)	0.707937±0.000008
12	5	upper Sargaevian, <i>An. alata</i> – <i>M. bogoslovskiy</i> Zone	<i>Ancyrodella pristina</i> , <i>An. rotundiloba alata</i> , <i>Mesotaxis asymmetricus</i> , <i>Klapperina ovalis</i> (Fig. S2: 14–15)	0.708162±0.000030
13	3	upper Sargaevian, <i>An. rotundiloba</i> – <i>africana</i> Zone – <i>An. alata</i> – <i>M. bogoslovskiy</i> Zone	<i>Mesotaxis asymmetricus</i> , <i>M. falsiovalis</i> , <i>Ancyrodella rotundiloba alata</i> (Fig. S4: 1–6)	0.707960±0.000011
14	6	middle Sargaevian; <i>An. rotundiloba</i> – <i>africana</i> Zone	<i>Icriodus nodosus</i> , <i>Ic. symmetricus</i> , <i>Ic. expansus</i> , <i>Mesotaxis falsiovalis</i> (Fig. S4: 7–11)	0.707948±0.000008
15	5	Timanian, <i>Po. pennatus</i> – <i>Po. ljaschenkoi</i> Zone	<i>Icriodus alternatus</i> , <i>Ic. nodosus</i> , <i>Polygnathus alatus</i> , <i>Po. ljaschenkoi</i> , <i>Po. dubius</i> , <i>Po. webbi</i> , <i>Ancyrodella pristina</i> , <i>A. binodosa</i> (Fig. S4: 12–15)	0.707896±0.000015
16	5	upper Givetian, Mullinian	<i>Ancyrodella prima</i> (Fig. S4: 16)	0.707918±0.000008
17	9	Eifelian, Mosolovian	<i>Polygnathus linguiformis alveolus</i> , <i>Pseudobipennatus</i> cf. <i>ziegleri</i> (Fig. S5: 12)	0.707780±0.000012
18	9	Eifelian	<i>Polygnathus</i> aff. <i>pseudofoliatus</i> (Fig. S5: 11)	0.707798±0.000012
19	4	Eifelian, Biyian	ramiform elements	0.708568±0.000020
20		lower Kungurian (control sample)	<i>Neostreptognathodus lectulus</i> (Fig. S3: 9)	0.707394±0.000010

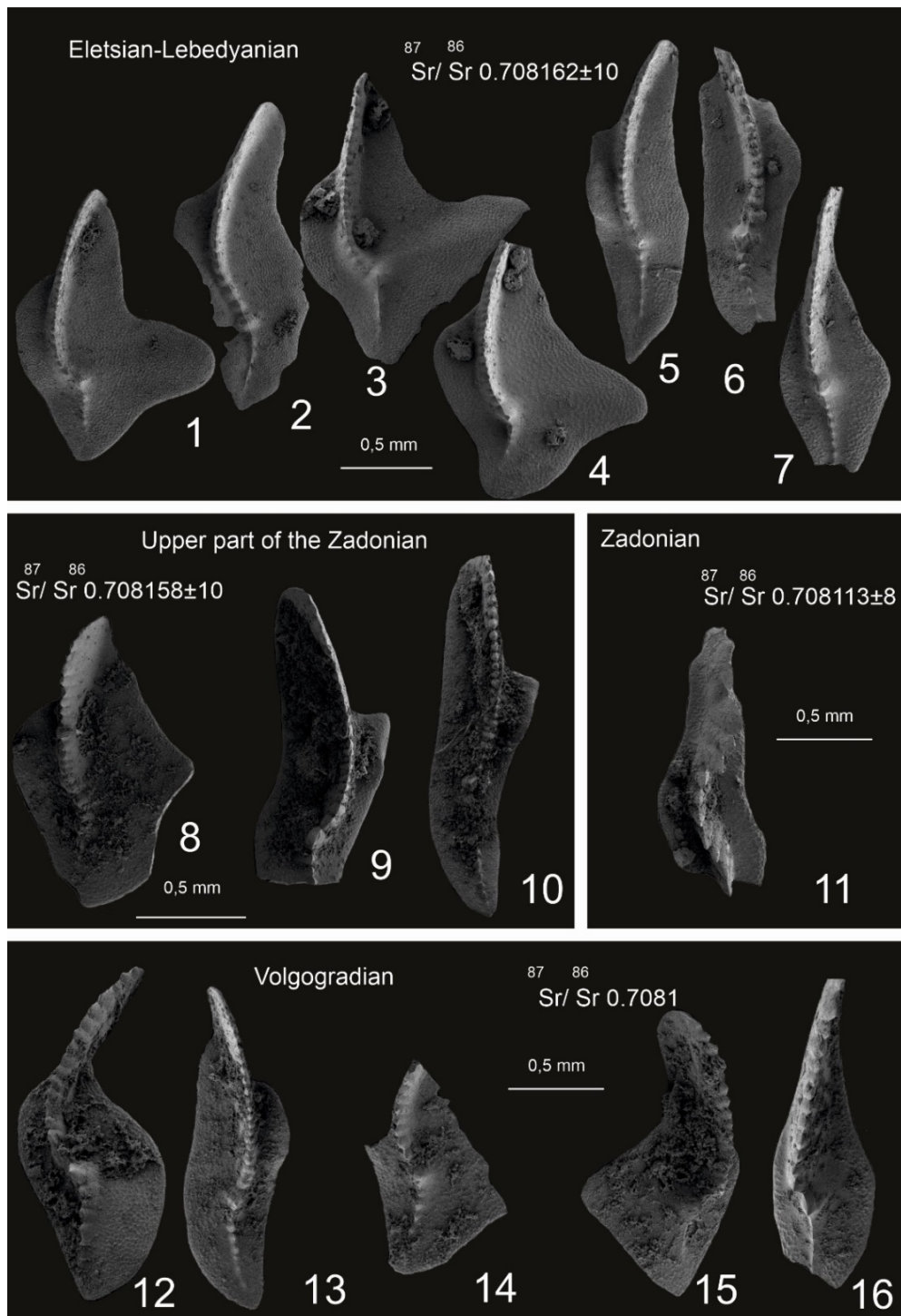


Figure S1. Famennian conodonts: 1, 3–4. *Palmatolepis lobicornis* Schülke, well no. 7, Elelsian–Lebedyanian, *rhomboidea* Zone – *marginifera* Zone; 2, 5–6. *Palmatolepis glabra glabra* Ulrich et Bassler, well no. 7, Elelsian–Lebedyanian, *rhomboidea* Zone – *marginifera* Zone; 7. *Palmatolepis minuta minuta* Branson et Mehl, well no. 7, Elelsian–Lebedyanian, *rhomboidea* Zone – *marginifera* Zone; 8. *Palmatolepis* sp., well no. 2, upper Zadonian, *crepida* Zone; 9–10. *Palmatolepis glabra glabra* Ulrich et Bassler, well no. 2, upper Zadonian, *crepida* Zone; 11. *Palmatolepis* sp., well no. 7, Zadonian, *crepida* Zone; 12. *Palmatolepis* aff. *regularis* Cooper, well no. 2, Volgogradian, *triangularis* Zone; 13. *Palmatolepis tenuipunctata* Sannemann, well no. 2, Volgogradian, *triangularis* Zone; 14. *Palmatolepis* cf. *superlobata superlobata* Branson et Mehl, well no. 2, Volgogradian, *triangularis* Zone; 15. *Palmatolepis superlobata superlobata* Branson et Mehl, well no. 2, Volgogradian, *triangularis* Zone; 16. *Palmatolepis minuta* Branson et Mehl, well no. 2, Volgogradian, *triangularis* Zone.

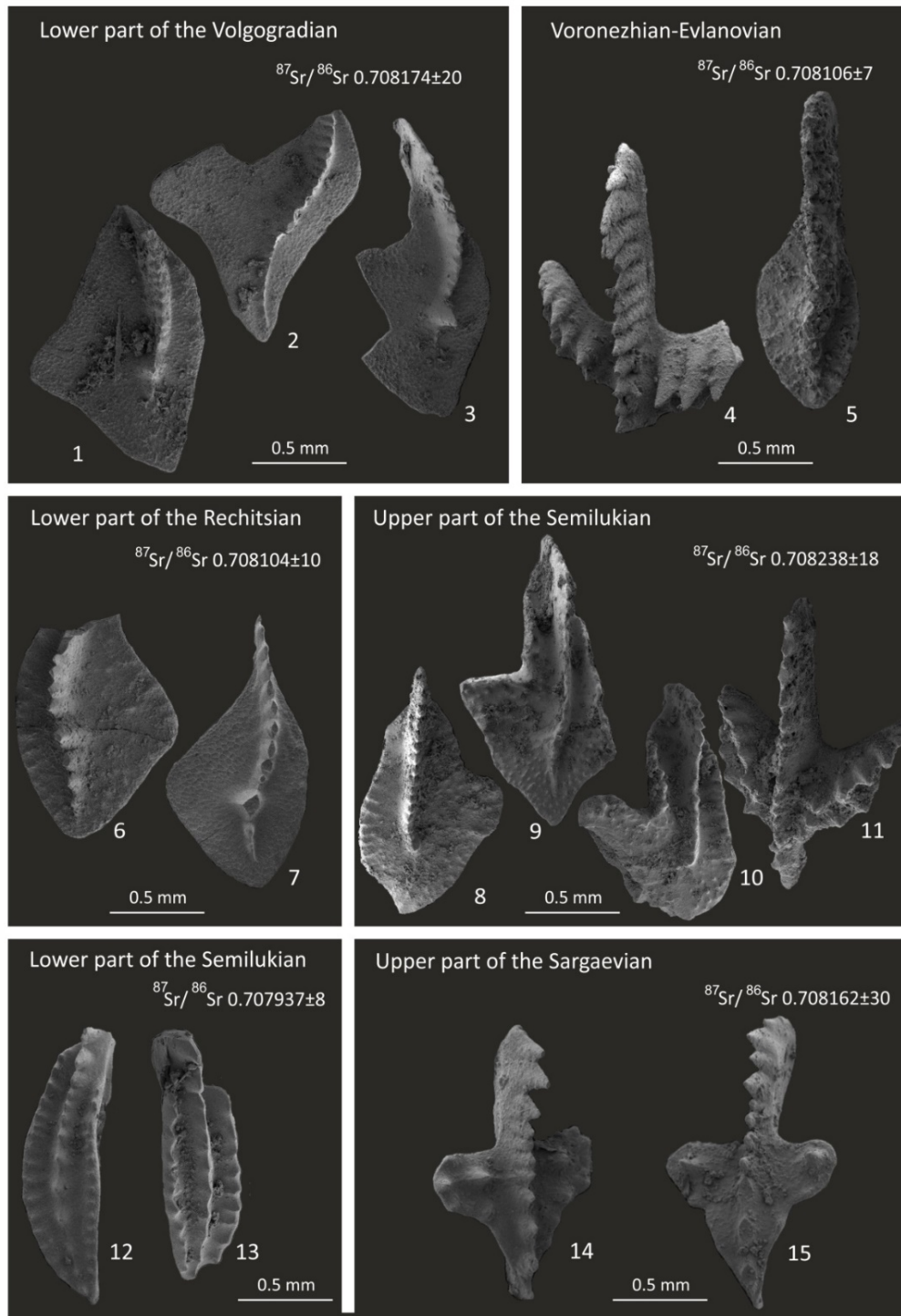


Figure S2. Famennian and Frasnian conodonts. 1, 3. *Palmatolepis* cf. *superlobata superlobata* Branson et Mehl, well no. 2, lower Volgogradian, *triangularis* Zone; 2. *Palmatolepis triangularis* Sannemann, well no. 2, lower Volgogradian, *triangularis* Zone; 4. *Ancyrodella ioides* Ziegler Morphotype 1, well no. 1, Voronezhian–Evlanovian, *elegantula–semichatovae* Zone – *juntianensis* Zone; 5 – *Palmatolepis* sp., well no. 1, Voronezhian–Evlanovian, *elegantula–semichatovae* Zone – *juntianensis* Zone; 6. *Palmatolepis* aff. *ljaschenkoae* Ovnatanova, well no. 2, lower Rechitsian, *elegantula–semichatovae* Zone; 7. *Palmatolepis* aff. *kireevae* Ovnatanova, well no. 2, lower Rechitsian, *elegantula–semichatovae* Zone; 8. *Palmatolepis* cf. *punctata* (Hinde), well no. 4, Upper Semilukian, *An. ancyrognathoides–Pa. orbicularis* Zone – *Pa. mucronata–amplificata* Zone; 9–10. *Palmatolepis proversa* Ziegler, well no. 4, upper Semilukian, *An. ancyrognathoides–Pa. orbicularis* Zone – *Pa. mucronata–amplificata* Zone; 11. *Ancyrodella nodosa* Ulrich et Bassler, well no. 4, upper Semilukian, *An. ancyrognathoides–Pa. orbicularis* Zone – *Pa. mucronata–amplificata* Zone; 12. *Polygnathus lingulatus* Ovnatanova, well no. 6, lower Semilukian, *Po. Efimovae–Pa. punctate* Zone. 13. *Polygnathus* aff. *grandidentatus* Aristov, well no. 6, lower Semilukian, *Po. efimovae–Pa. punctate* Zone; 14–15. *Ancyrodella pristina* Khalymbadzhia et Chernysheva, well no. 5, upper Sargaevian, *An. alata–M. bogoslovskiyi* Zone.

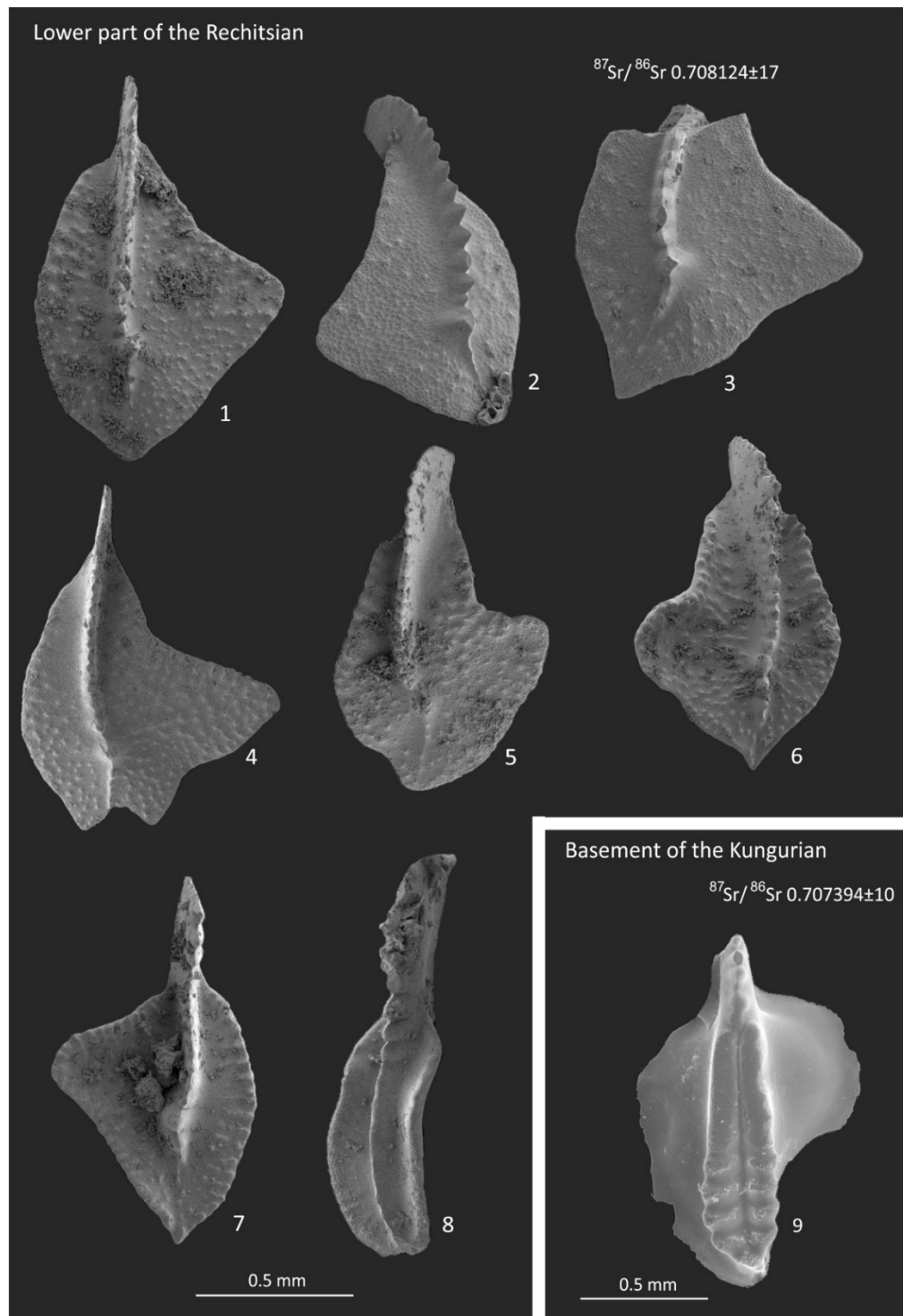


Figure S3. Frasnian conodonts. 1, 3. *Palmatolepis hassi* Muller et Muller, well no. 4, lower Rechitsian, *elegantula–semichatovae* Zone; 2. *Palmatolepis jamieae* Ziegler et Sandberg, well no. 4, lower Rechitsian, *elegantula–semichatovae* Zone; 4. *Palmatolepis nasuta* Muller, well no. 4, lower Rechitsian, *elegantula–semichatovae* Zone; 5–6. *Palmatolepis plana* Ziegler et Sandberg, well no. 4, lower Rechitsian, *elegantula–semichatovae* Zone; 7. *Palmatolepis* aff. *gyratus* Kuzmin et Melnikova, well no. 4, lower Rechitsian, *elegantula–semichatovae* Zone; 8. *Polygnathus* sp., well no. 4, lower Rechitsian, *elegantula–semichatovae* Zone; 9. *Neostreptognathodus lectulus* Chernykh, Mechetlino section, layer 12, lower Kungurian.

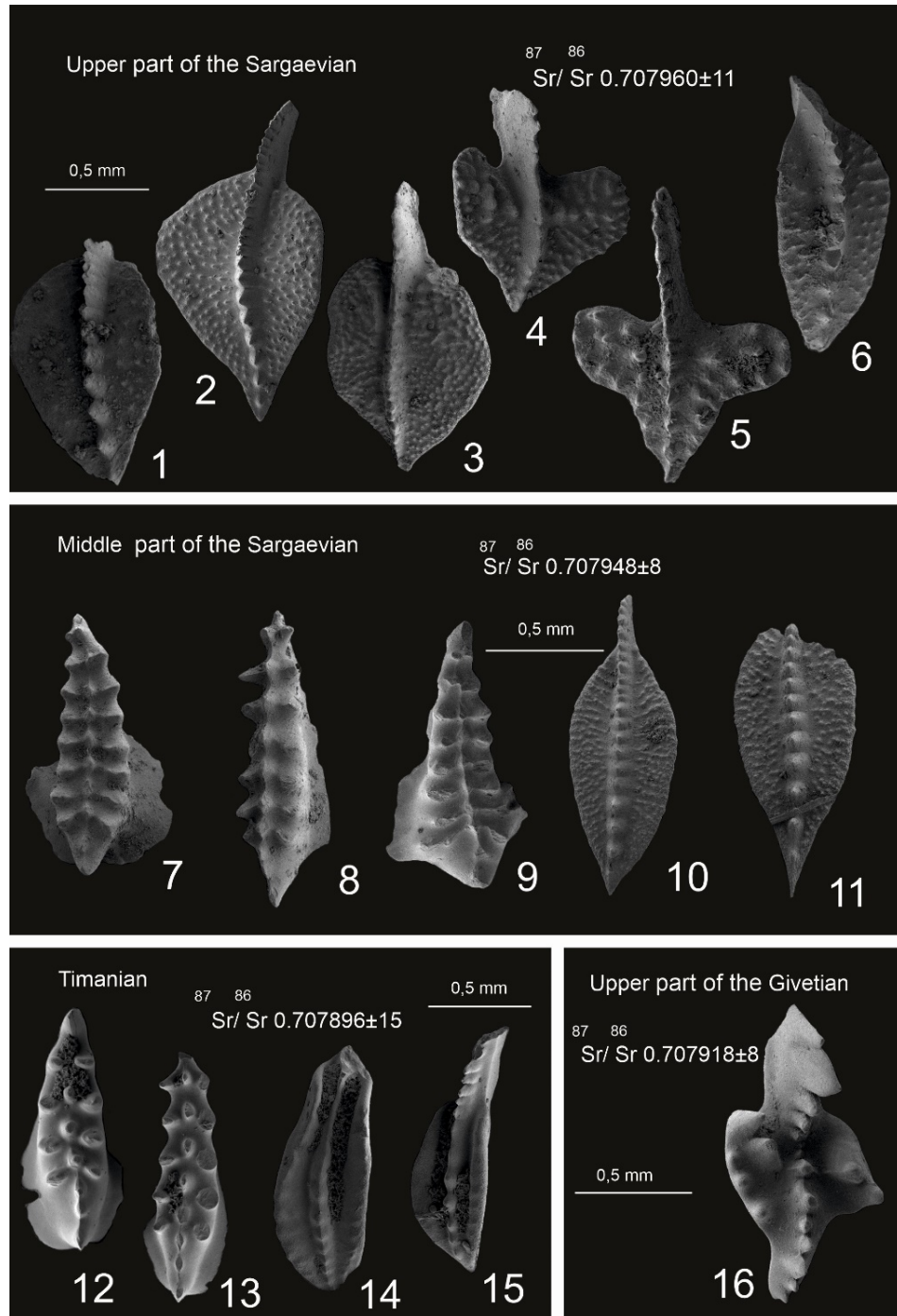


Figure S4. Frasnian and Famennian conodonts. 1. *Mesotaxis falsiovalis* Sandberg, Ziegler, Klapper, well no. 3, upper Sargaevian, *An. rotundiloba–africana* Zone – *An. alata–M. bogoslovskiy* Zone; 2–3. *Mesotaxis asymmetricus* (Bischoff et Ziegler), well no. 3, upper Sargaevian, *An. rotundiloba–africana* Zone – *An. alata–M. bogoslovskiy* Zone; 4–5. *Ancyrodella rotundiloba alata* Glenister et Klapper, well no. 3, upper Sargaevian, *An. rotundiloba–africana* Zone – *An. alata–M. bogoslovskiy* Zone; 6. *Mesotaxis falsiovalis* Sandberg, Ziegler et Klapper, well no. 3, upper Sargaevian, *An. rotundiloba–africana* Zone – *An. alata–M. bogoslovskiy* Zone; 7. *Icriodus nodosus* (Hiddle), well no. 6, middle Sargaevian; *An. rotundiloba–africana* Zone; 8. *Icriodus symmetricus* Branson et Mehl, well no. 6, middle Sargaevian; *An. rotundiloba–africana* Zone; 9. *Icriodus expansus* Branson et Mehl, well no. 6, middle Sargaevian; *An. rotundiloba–africana* Zone; 10–11. *Mesotaxis falsiovalis* Sandberg, Ziegler et Klapper, well no. 6, middle Sargaevian; *An. rotundiloba–africana* Zone; 12–13. *Icriodus alternatus* Branson et Mehl, well no. 5, Timanian, *Po. pennatus–Po. ljaschenkoi* Zone; 14. *Polygnathus alatus* Huddle, well no. 5, Timanian, *Po. pennatus–Po. ljaschenkoi* Zone; 15. *Polygnathus ljaschenkoi* Kuzmin, well no. 5, Timanian, *Po. pennatus–Po. ljaschenkoi* Zone; 16. *Ancyrodella prima* Khalymbadzhia et Chernysheva, well no. 5, Upper Givetian, Mullinian.

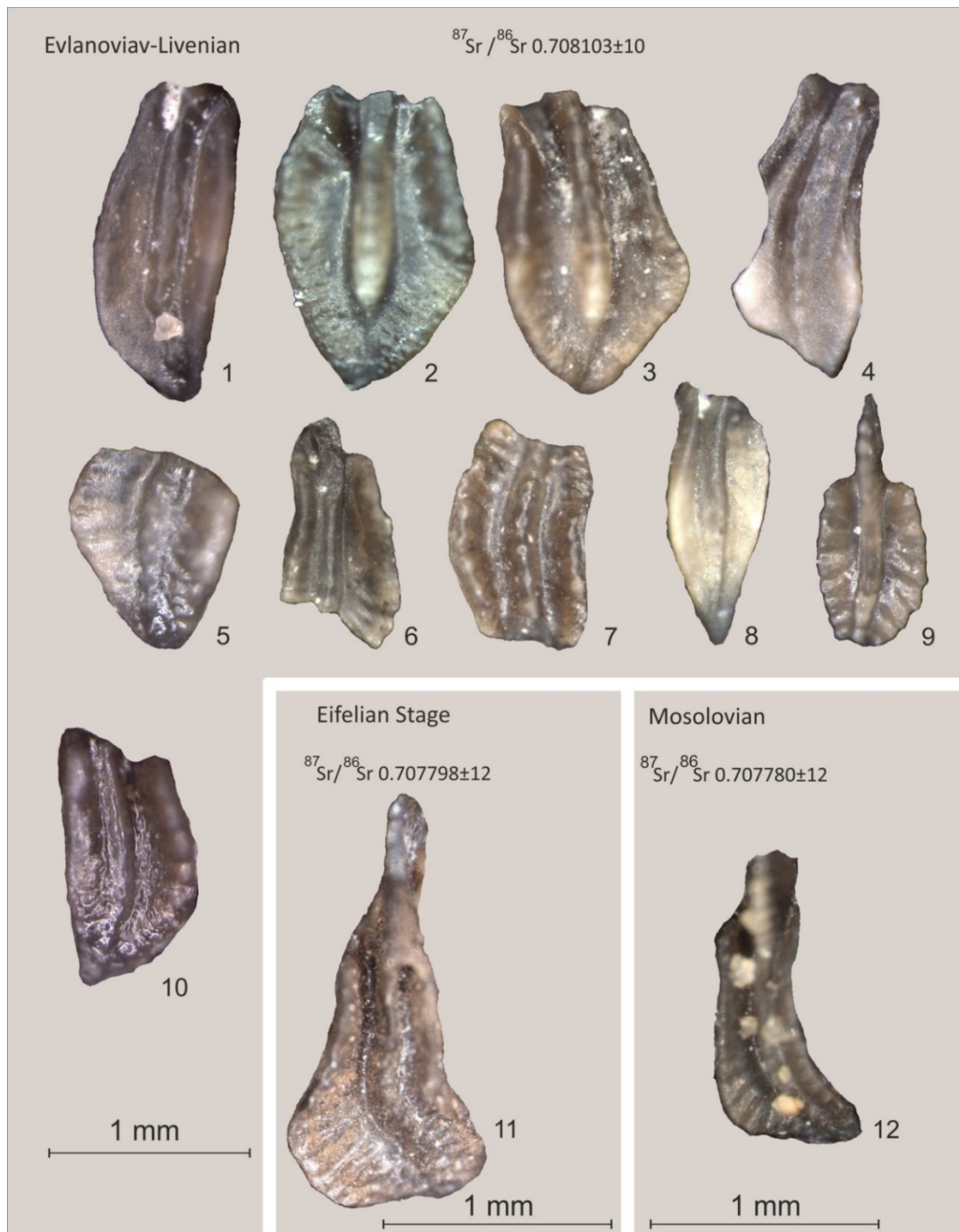


Figure S5. Eifelian and Frasnian conodonts: 1. *Polygnathus politus* Ovnatanova, well no. 8, Evlanovian–Livenian, *juntianensis* Zone – *linguiformis* Zone; 2–3. *Polygnathus komi* Kuzmin et Ovnatanova, well no. 8, Evlanovian–Livenian, *juntianensis* Zone – *linguiformis* Zone; 4. *Polygnathus* cf. *lodinensis* Pölsler, well no. 8, Evlanovian–Livenian, *juntianensis* Zone – *linguiformis* Zone; 5. *Polygnathus* cf. *costulatus* Aristov, well no. 8, Evlanovian–Livenian, *juntianensis* Zone – *linguiformis* Zone; 6. *Polygnathus* cf. *krestovnikovi* Ovnatanova, well no. 8, Evlanovian–Livenian, *juntianensis* Zone – *linguiformis* Zone; 7. *Polygnathus* cf. *aequalis* Klapper et Lane, well no. 8, Evlanovian–Livenian, *juntianensis* Zone – *linguiformis* Zone; 8. *Polygnathus politus* Ovnatanova, well no. 8, Evlanovian–Livenian, *juntianensis* Zone – *linguiformis* Zone; 9. *Polygnathus* aff. *pennatus* Hinde, well no. 8, Evlanovian–Livenian; 10. *Polygnathus* cf. *webbi* Stauffer, well no. 8, Evlanovian–Livenian, *juntianensis* Zone – *linguiformis* Zone; 11. *Polygnathus* aff. *pseudofoliatus* Wittekindt, well no. 9, Eifelian; 12. *Polygnathus* cf. *linguiformis alveolus* Weddige, well no. 9, Mosolovian.

Стронциевая изотопная стратиграфия среднего и верхнего девона: данные по конодонтам из центральной части Волго-Уральской нефтегазоносной провинции

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Представлены первые данные по изотопному составу стронция ($87\text{Sr}/86\text{Sr}$) для средне- и верхнедевонских отложений центральной части Волго-Уральской нефтегазоносной провинции, полученные на основе анализа рамиформных элементов конодонтовых аппаратов. Стратиграфическое положение большинства образцов определено по содержащимся в них платформенным конодонтам. Значения $87\text{Sr}/86\text{Sr}$ демонстрируют хорошую согласованность с глобальной стронциевой кривой, что указывает на устойчивую связь исследуемого региона с Мировым океаном на протяжении среднего и позднего девона. Полученные данные подтверждают высокую степень стратиграфической полноты регионального разреза, несмотря на многочисленные перерывы осадконакопления и частое чередование доломитовых, терригенных и карбонатных отложений.

Ключевые слова: конодонты, девон, изотопы стронция ($87\text{Sr}/86\text{Sr}$), Волго-Уральская нефтегазоносная провинция

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Мы выражаем глубокую благодарность редакторам и анонимным рецензентам, чьи комментарии и предложения значительно улучшили статью.

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