Geochemical variations in the Upper Kazanian (Middle Permian) stratotype section, Russia

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Abstract. The present paper shows elemental and carbon and strontium isotope composition of the Upper Kazanian (Middle Permian) stratotype section Pechishchi, Russia. A new version of Noinsky’s cycles scheme has been obtained for Martinet and Sougy’s Diagram types of carbonates, with the geochemical indices values changing within marine, evaporate and clastic beds. The δ13C values vary within interval 0−10‰ V-PDB with a mean value 6.2 ‰ V-PDB. The negative excursions of δ13C values (with amplitudes 2-8 ‰) are assigned as significant land-derived sedimentary inputs. The values of 87Sr/86Sr ratio in the data set of 17 samples change from 0.707267 to 0.707417 (mean value 0.70734). On standard 87Sr/86Sr curve these values correspond to the interval 273 – 268 Ma.

1. Introduction

The stratotype of the Upper Kazanian substage is exposed on the south bank of the Volga River opposite Kazan city. According to the Russian General Stratigraphic Scale (RGSS), the Permian in the study area is subdivided into three stratigraphic units: (i) the fully marine succession (Cisuralian Series); (ii) the marine-continental (transitional) succession represented by the Ufimian, Kazanian and Urzhumanian stages; (iii) the continental succession consisting of the Severodvinian and Vyatkian stages [1]. The Kazanian stage is correlated with the Roadian (middle Permian) of the International Startigraphic Chart [2, 3]. In stratotype region, the middle Permian deposits are widely distributed and well exposed in numerous outcrops due to high relief (up to 200 m).

The lower boundary of the Kazanian is clearly defined by the marine Kazanian succession, which unconformably overlies either the Sakmarian dolomites or the Ufimian continental red beds. The boundary between the Lower and Upper Kazanian and lower part of succession (units 1-7) is exposed in the slope of the bank between villages of Pechishchi and Naberezhnye Morkvashi [2]. The overlying beds are quite well-exposed on the south bank of the Volga River near the village of Pechishchi, near the mouth of Cheremushka Gully, and in the slopes of the Telegraphny Gully and Kamennyi Gully. The Kazanian-Urzhumanian boundary is most accessible in the Cheremushka Gully. M.E.Noinsky was first who described the section, which consists of eight series or members, attributed the section to three sedimentary cycles [4, 5]. Detailed paleontological analysis of the section was provided by Solodukho and Tikhvinskaya (1977) [2]. They considered the cycles as biostratigraphic horizons and reattributed them to four complexes. These horizons of the Pechishchi section are currently considered as beds according to the Russian Stratigraphic Code, and reassigned geographical names [2]. This Kazanian succession is well elaborated, while its geochemical characteristics are still poorly known [2]. No advanced geochemical study was presented until now.
The Upper Kazanian (middle Permian) carbonate strata of the East European Platform from the Pechishchi section near Kazan city have yielded a block of rocks to reconstruct elemental and isotopic composition, variations and trends. The present paper used the bulk and isotope geochemistry analyzed by X-ray fluorescence spectrometry and mass-spectrometry. The distribution of major and trace elements, δ\(^{13}\)C and \(^{87}\)Sr/\(^{86}\)Sr were considered in this paper.

2. Object

The description of the Upper Kazanian section is based on data taken by all previous researchers [1-5]. The section is composed of 31 beds grouping up in the Prikazan beds (no.1-13), the Pechishchi beds (no.14-21), the Verkhnyi Uslon beds (no.22-28) and the Morkvashi beds (no.29-31) (Figure 1). The Prikazan beds include A (Yadrenyi Kamen: beds no.1-8) and B (Sloisty Kamen: beds no.9-13) members. The Pechishchi beds consist of C (Podboi: beds no.14-16), D (Seryi Kamen) and E (Shikhany: bed no.21) members. The Verkhnyi Uslon beds include F (Opoki: beds no.22-25) and G (Podluzhnik: beds no.26-28) members. The Morkvashi beds comprise H (Perekhodnaya: beds no. 29-31) member. All member names were taken from [4, 5].

The beds up the section are characterized by the following lithologies:

**Bed no.1.** Dolostone: tan, probably argillaceous, preserving horizontal gently undulating lamination, riddled with characteristic vermiform voids. Thickness 2.25 m.

**Bed no.2.** Dolostone: pale grey, weathers yellowish, calcareous, thick-bedded, tight and hard. Samples show bioclastic mudstone texture with predominantly horizontal to random orientation of bioclasts. Fine poorly preserved plant detritus may be present. Thickness 0.60 m.

**Bed no.3.** Dolostone: pale grey, weathers yellowish, indistinctly bedded, massive, of medium hardness. With bioturbated bioclastic mudstone-wackestone and packstone texture (bioclasts include brachiopods and bivalves). Thickness 0.70 m.

**Bed no.4.** Dolostone: pale grey, hard and tight, locally vuggy, with rare Cancrinella cancrini (Vern.), retains bioclastic texture (packstone) and lenticular lamination with shell pavements (including fragments and whole valves of Aulosteges fragilis (Netsch.). Base is possibly erosional. Up the bed fissile to thin-bedded, retaining bioclastic wackestone texture and wavy lamination. Thickness 1.50 m.

**Bed no.5.** Dolostone: massive to weakly laminated bioclastic wackestone with rare in situ brachiopods Cancrinella cancrini (Vern.), Rhynchoalora geinitziana (Vern.), Cleiothyridina pectinifera (Sow.). At the top, the rock is vuggy and locally thin-bedded. The unit stands out in the outcrop due to its monolithic appearance. Thickness 0.60 m.

**Bed no.6.** Dolostone: yellowish grey, fissile to thin-bedded, with finely to microcrystalline fabric (5–50 μm), microporous, locally vuggy, relatively soft. Moderately bioturbated to laminated bioclastic packstone and wackestone. Bedding / fissility planes show laminae enriched in charophyte stalks and laminae dominated by brachiopod fragments. Some brachiopods are preserved in life position (Cancrinella). Brachiopod coquinas (storm beds) at 0.20 m, 0.30 m, and 0.40 m above the base. These
coquinas are disrupted by burrowing. Some bedding planes show darker coloured gently plunging and randomly curved burrows identified as *Planolites*. Thickness 0.30 m.

Bed no. 7. Dolostone: calcareous, moderately argillaceous, yellowish grey with bluish mottles, fine-grained, rich in void-filling bluish large celestine crystals. Laterally grading into grey coloured recessive fissile calcareous marl. The marl facies contain cm-thick resistant limestone beds and lenses with shell coquinas and erosional surfaces indicative of tempestite rhythmicity. Macrofossils: bivalves, brachiopods of genera *Cancrinella, Aulosteges, Stenoscisma, Crurithyris*, and branching bryozoans. Thickness 0.40 m.

Bed no. 8. Dolostone to limestone: bluish grey, fine-grained, weathering rusty. The lower part is hard and monolithic, locally composed of weakly fissile bluish grey limestone. This limestone shows low-contrast sedimentary rhythmicity (bioclastic-micritic graded beds). The upper part is more argillaceous and slightly more recessive. Fossils: ostracods, fragmented brachiopods *Cancrinella cancini* (Vern.), crinoid ossicles, ichthyolites, charophyte remains. Conodonts *Stepanovites meyeni* Kozur et Movsh.
Bed no. 9. Dolostone: pale grey, calcareous, fine-grained, tight and hard, with locally preserved bioclastic texture. The unit consists of four beds. The lower two beds contain unsorted, up to 6 mm in size, skeletal material that locally dominates the rock texture. The lower 0.5 m of the unit locally preserves graded bioclastic beds indicating its facies unity and conformable relation with the underlying bed no. 8. The upper part contains gypsum nodules and cavities left by their dissolution. Fossils: bivalves of the genera *Nuculana, Lithophaga, Pseudobakewellia, Schizodus, Permophorus, Pseudomonotis, Solemya, Alula*; brachiopods of the genera *Cancrinella, Pinegathyris,* and *Beecheria*; branching bryozoans and conodonts *Stepanovites meyeni Kozur et Movsh.* Thickness 0.20 m.

Bed no. 10. Dolostone: yellowish grey, hard and tight, breaking along smooth to gently conchoidal surfaces, locally showing thin undulating bedding. No fossils. Thickness 0.60 m.

Bed no. 11. Dolostone: pale grey, calcareous, microporous, soft, finely crystalline, medium bedded, preserving non-sorted (up to 2 mm in size) bioclasts showing predominant horizontal orientation. Thickness 1.40 m.

Bed no. 12. Dolostone: dull grey, finely crystalline, of medium hardness, cavernous, with rusty ferruginous crusts produced on weathered surfaces and geodes of ferruginised calcite crystals. Unconfirmed presence of poorly preserved biomolds up to 1.5 mm in size. Polished slabs show calcimudstone texture with variously preserved horizontal microlamination and vertical *Scolithos* burrows, at the top more bioturbated with small curved burrows. Locally, dolostone grades into dark grey crystalline limestone likely representing dedolomite. Thickness 1.70 m.

Bed no. 13. Dolostone: very pale grey (almost white), finely crystalline and microporous, soft, retaining fine lamination with occasional preservation of buckled and “teepee” structures and rip-up intraclastic breccias. The tidal-flat desiccation and buckled features become more important towards the unit top. Rare small (less than 0.5 mm) bioclasts. Celestine-filled and empty vugs after dissolved anhydrite / gypsum. The bed top is textured by desiccation polygons and root-like branching structures. No distinct alluvial shale coatings or stringers at the top despite the overlying shale.

Bed no. 14. Shale: greenish to brownish grey, ductile, intensely slickensided with coaly detritus and fish scales (*Palaeoniscum* sp.). From base to top the bed can be divided into three parts: 0–0.05 m – greish brown shale with coaly detritus, rare fish scales, and poorly preserved shell fragments; small fragments of dolostone in the very base pointing to a moderate weathering of the underlying bed; 0.05–0.15 m – pigeon grey shale with brownish partings; 0.15–0.30 m – dark brownish grey shale with admixture of sooty material, intensely slickensided from the top. Thickness 1.00 m.

Bed no. 15. Dolostone breccia: rubble of various hardness, non-bedded, locally cemented by calcite and partly converted into dedolomitic limestone. Polished slabs from dolostones fragments show horizontal lamination and several levels containing presumable *Scolithos* burrows. Thickness 2.50 m.

Bed no. 16. Dolostone: dull buff, probably argillaceous, microporous, of medium hardness, thin-bedded, retaining thin sedimentary lamination and calcimudstone texture with rare small biomolds; breaking into rhombohedral blocks. Contains small (2–3 mm) ovoid nodules of sparry calcite. The
rock is locally dedolomitised into dark grey secondary calcite. A cavernous coarsely crystalline secondary limestone was also observed. Thickness (visible) 0.35 m. Here the upper 0.35 m of bed 16 is described as hard pale yellowish grey fine-grained dolostone (17.65–17.75 m) grading upwards into grey thin-bedded fine-grained dolostones with molds after bivalve shells (17.75–18.00 m). In polished slabs, retains fine-grained laminated ooid grainstone texture.

**Bed no. 17.** Dolostone: grey to yellowish, buff, very fine grained and finely crystalline (0.2 mm) idiotopic, seemingly impregnated with organic matter, microporous, relatively soft; locally retains ooidal and bioclastic-ooidal texture and inclined to horizontal lamination sets; the ooids are sometimes internally leached. Brecciation and small (up to 8 mm) pebbles of carbonate rocks in the middle (1.0–1.25 m from base). The upper part above the pebble horizon shows numerous bivalves and vugs. Numerous macrofossils, preserved as biomolds: gastropods *Goniastra* and *Baylea*, bivalves *Schizodus*, nautiloids, brachiopods *Aulosteges wangenheimi* (Vern.), *Cleiothyridina pectinifera* (Sow.), and *Beecheria* sp., fenestellid and branching bryozoans, and crinoid ossicles. The erosional base (ravinement) locally hosts conglomerate with small dolostone and dolomarl pebbles. At the top buff dolostone, moderately argillaceous. Thickness 0.90 m, off-station locally increases to 2.0 m.

**Bed no. 18.** Dolostone: argillaceous and buff-coloured, microporous, thick-bedded and grading at the top into thinbedded, showing characteristic rhombohedral jointing and lenticular pattern. In polished slabs, vague horizontally trending features may be an expression of primary lamination or lithostatic compaction. Diverse macrofauna, encountered only in the uppermost part: the bivalves (molds) *Pseudomonotis* (Trematiconcha) noinskyi (Lich.), *Pseudomonotis* (Pseudomonotis) permianus Masl., *Solemya* (Janeia) biarmica (Vern.), *Paralleledon kingi* Vern., spines and shell fragments of *Cancrinella*, fish scales of *Platysomus* sp., *Acentrophorus varians* Kirkby, *Kasanichthys* sp., the inarticulate brachiopods *Orbiculoidea konincki* (Gein.), and *Conularia hollebeni* (Gein.) (the only occurrence of conularians in the section), branched trace fossils *Palaeophycus insignis* (Gein.). The unit seems to laterally grade into fine-grained (‘sandstone-like’) dolostones similar to packages above and below. Thickness 2.10 m.

**Bed no. 19.** Dolostone: grey, very fine-grained (‘sandstone-like’), locally mottled, medium to thick bedded. Nodules and secondary open-space large crystals of gypsum. From base to top: grey and yellow-mottled, weakly fissile dolostone with faintly laminated mudstone texture (0.00–0.25 m); brownish grey thick-bedded dolostone with fissile top, partly cross-laminated, showing fine-grained bioclastic-oolitic grainstone texture (0.25–2.10 m). Two bivalve horizons at 0.30–0.40 m and 1.35–1.40 m above the base. Gastropod and bivalve molds are locally abundant, some of them filled by gypsum and chert. Local presence of 1–2 m thick partly dolomitised buildups with bryozoan framework and massive ooidal-bioclastic matrix. Frame-building bryozoans: *Tabulipora ordinata* Moroz., *Fenestella permulta* Moroz., and other species. Other fauna in buildups: *Aulosteges wangenheimi* (Netsch.), *Pseudomonotis garforthensis* (King), foraminifers. Thickness 1.70 m.

**Bed no. 20.** Dolostone: grey, fine-grained, tight to locally vuggy, partly chertified and dedolomitised into a crystalline limestone. The base yields rare bivalves *Nuculana kasanensis* (Vern.), *Pseudomonotis* (Ps.) permianus Masl., *Pseudobakewellia ceratophagaformis* Noin., the brachiopods *Cancrinella cancini* (Vern.), *Cleiothyridina pectinifera* (Sow.), *Beecheria netschajewi* Grig., and
branching bryozoans. The upper part (0.85–1.30 m) bears numerous ellipsoidal chert nodules (0.30 x 0.40 m) and quartz druses; the 40 cm at the top is notably vuggy, with gypsum nodules.

**Bed no. 21.** Dolostone: white to pale grey, unevenly crystalline, porous, relatively hard, with thin buckled lamination, rich in granules, nodules and flakes of gypsum (originally anhydrite). The latter locally dominates the rock in the upper part of the unit. Some rock slabs show, typical for sabkha, chickenwire fabric with gypsum nodules displacing and contorting dolomite partings. The rock is vuggy and soft where the gypsum is weathered out. Gypsum nodules contain celestine crystals. Common elliptical chert nodules. The bed top textured by desiccation polygons.

**Bed no. 22.** Dolostones and marls with faint buckled lamination and local rip-up breccia. Base unconformable, erosional. The unit can be divided into four parts, from base to top: (i) conglomerate of flat subrounded clasts (up to 1 cm in size) of marls and shales in silty shale matrix, up to 20 cm in thickness, grading laterally to dolomarl with floating dolostone clasts, thickness 0.10 m; (ii) dolomarl: soft pale, yellowish grey, locally with breccia fabric, in polished slabs showing faint buckled lamination, thickness 0.70 m; (iii) dolostone: yellowish grey, resistant, with vugs and rusty staining in 25 cm from the base, thickness 0.40 m; (iv) alternation of pale grey dolostones and dark grey dolomarls forming 2–3 cm thick laminae; the dark grey laminae contain sooty organic matter, thickness 0.20 m.

**Bed no. 23.** Dolostone: grey, argillaceous, locally with fine sand admixture, fine-grained, with faint undulating lamination, with rare bioclasts, with shale 2–3 cm thick seams in the middle. Polished slabs from the base show very fine-grained laminated oolitic texture with rare bioclasts. The main part of the bed above the base shows mudstone texture. No fossils. Thickness 0.75 m.

**Bed no. 24.** Dolomarl-dolostone alternation: yellowish grey, recessive dolomarls are darker and resistant dolostones are lighter coloured. Dolostones are mostly soft, locally cherty, include 2–3 cm thick beds of harder fragile partly cherty dolostones. A 10 cm thick cherty stromatolithic dolostone at the top. Polished slabs show fine grainy texture and levels of buckled lamination with teepee structures.

**Bed no. 25.** Dolostone: grey, argillaceous, very fine-grained, finely fractured, with ferruginised fracture planes, more argillaceous and grading to sandstone at the top. The upper sandstone locally hosts numerous bivalve and brachiopod valves. Bivalves: *Pseudobakewellia, Pseudomonotis*. Brachiopods: *Cancrinella, Rhynchopora, Cleiothyridina*. Foraminifers: *Glomospira, Ammodiscus, Pseudoammodiscus*. Thickness 2.50 m.

**Bed no. 26.** Dolostone: pale grey, argillaceous, thick-bedded, with chert nodules. Bivalves preserved as casts and impressions: *Nuculana, Schizodus, Netschajewia, Pseudomonotis*. Brachiopods: *Cancrinella, Beecheria, Spiriferellina, Odontospirifer*. Fish scales and conodont elements of the genus *Kamagnathus*. Thickness 5.00 m.

**Bed no. 27.** Dolostone: pale grey, microcrystalline, locally clotted, with chert horizons; alternation of massive and laminated intervals, the latter showing ripple marks on bedding planes. Cherts preserve
sedimentary texture of birds-eye micritic laminite; cherts at 2.80–2.85 m from the base contain bivalves and probably foraminifers. Thickness 3.00 m.

Bed no. 28. Dolostone: pale grey, microcrystalline, fragile, massive to microlaminated, rich in seams and nodules of white and pinkish gypsum; vuggy and locally disintegrated into powder where the gypsum is weathered out. The top is textured by desiccation polygons; the uppermost 0.15 m contains solution breccias and flat-pebble intraclastic conglomerates. Thickness 3.00 m.

Bed no. 29. Dolomarl: mottled yellowish grey, microcrystalline (dolomudstone), with dolostone conglomerates in basal 10–20 cm. The upper half shows low-contrast alternation of recessive dolomarls and resistant argillaceous dolostones. The rock shows fine undulating lamination defined by slim shale partings. A thin (3–4 cm) graded bed enriched in fine-grained (0.1–0.3 mm) bioclasts and polymeric sand at 0.6–0.7 m above the base. Fossils: conchostracans, non-marine ostracods *Palaeodarwinula*, *Prasuchonella*, and other genera, non-marine bivalves *Palaeomutela*, fish scales, and plant detritus. Thickness 4.20 m.

Bed no. 30. Dolostone: pale grey, microcrystalline, thick-bedded, partly sandy and argillaceous, with fine undulating lamination, slickensided. The basal part shows microbrecciation in polished slabs and contains the abundant non-marine bivalves *Palaeomutela*. The upper one-half of the unit hosts abundant marine fossils: the bivalves *Lithophaga* (= *Modiola*), *Schizodus*, *Pseudomonotis*, the brachiopods *Cancrinella*, *Beecheria*, and the conodonts *Kamagnathus volgensis* Chern. Thickness 2.00 m.

Bed no. 31. Dolomarl with interlayers of dolostone and packbreccia. In 15 cm above the chalcedony-quartz rhomb horizon, there is a 5–6 cm thick packbreccia of subrounded grey-coloured dolomite clasts embedded in red-coloured argillaceous matrix. The top of this breccia locally shows colour inversion to red clasts and gley matrix. Red-coloured clasts are also encountered at the base of this breccia. The breccia is overlain by a rounded-grain intraclastic calcarenite (1–2 cm), which is in turn succeeded by red shale and a second horizon of fine-grained argillaceous-dolomitic breccia, very similar in its appearance to the lower horizon. Thickness 0.80 m.

The section was probed at the all 31 beds (120 samples) for elemental and isotopic analysis.

3. Methods
XRF spectrometry is an analytical laboratory technique used to detect the presence of specified elements in a sample material and subsequently determine the concentration of those elements present. Bulk chemical analysis of samples was carried out using energy dispersive X-ray fluorescence method (EDXRF) on a fully-automated S2 RANGER (Bruker ASX) spectrometer having Pd-tube as X-ray source and silicon drift detector. Preparing of sample for analysis included its crushing in mill for 5 minutes to a particle size of about 40-50 μm; compaction with boric acid in a press with a force of 200 kN to get a tablet with a very smooth surface. Next, the tablet was placed in the instrument for analysis. The result can be received as a percentage of the components or in terms of their oxides in a
concentration range from 100 % to ppm- level. The analytical precession is better than 5% for major and trace elements.

The isotope mass spectrometer Delta V Plus (Thermo Fisher Scientific, Germany) with the prefix Gas Bench was used to determine the isotopic composition of carbon in carbonates. The sample of 200 μg was placed in a special flask, and tight-fitting lid with a septum. Further flask was placed in an auto sampler at a temperature 72˚C. Each sample was purged with helium for 10 minutes to remove the air from the flask. Then 1 ml of 100% purified phosphoric acid was dripped in the flask. It was hold 4 hours at a temperature 72˚C for a complete passage of the displacement reaction of carbon dioxide from carbonates by the phosphoric acid. Then fifteen portions of formed gas (1ml each portion) was picked out by autosampler, dried and passed through a chromatography column Pora Plot Q at a temperature 72˚C and at last sent for analysis in the mass spectrometer. Mass spectrometric analysis was provided by carbonate standard NBS-18 and gas portion with standard isotope composition and calibration technique using to calculate isotope composition of each sample.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio determination was performed in the laboratory of isotope geochemistry and geochronology of IGEM RAS (Moscow). The 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). The chemical preparation was conducted in a dust-free environment of a clean room. A sample of 0.01 g of a finely divided probe was dissolved in 10% acetic acid at room temperature, and 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 [6]. The effect of mass discrimination was taken into account by the normalization method to the isotopic ratio $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ 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; during the experiments the average value of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio according to the results of independent parallel measurements was 0.710250 ± 20 (2σ, n = 8).

4. Results and Discussion
The general geochemical characteristics are shown in Figure 2. The oxides forming silicate minerals of the carbonate rocks are considerably low, except those of the rocks with dominating clastic composition. However, regarding the values of $\text{Al}_2\text{O}_3$ relative to those of $\text{SiO}_2$ the carbonate rocks are characterized by abundant free quartz (the ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ is in range 2.98-10.85 with average value 4.33) (Figure 2). The presence of free quartz suggests shallow marine conditions. The higher silica content than those given by [7] 0.32-9.72% (excluding beds with clastic dominant input) can be attributed to the presence of $\text{SiO}_2$ in the form of quartz grains which were microscopically identified.
The consistent distribution of $\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}$ and occasionally $\text{K}_2\text{O}$ suggests their presence in the form of alumino-silicate minerals.

Corbel [8] proved that there is an increase in $\text{SiO}_2$ content towards the warmer climatic zone while Dekimpe et al [9] noted that with increasing pH there is a decrease in the silica content. Accordingly the carbonate sediments were mostly deposited under relatively warm alkaline conditions.

$\text{Al}_2\text{O}_3$ is more soluble in acidic medium than $\text{SiO}_2$ and in neutral medium (5-6 pH) $\text{Al}_2\text{O}_3$ is insoluble whereas $\text{SiO}_2$ retains its solubility. In alkaline medium the two solubilities meet. The constituent distribution of both $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ favored their occurring in contemporaneous deposition suggesting that the pH of the medium was 7.8 to 8.0 [10].

$\text{K}^+$ ions are preferentially adsorbed by the fine-grained particles of the sediments in comparison with $\text{Na}^+$ [11] therefore the slight predominance of $\text{K}_2\text{O}$ contents over $\text{Na}_2\text{O}$ contents in section could be understood.

The ferric oxide contents show to a great extent consistent distribution with those of $\text{SiO}_2$, $\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}$, $\text{K}_2\text{O}$ suggesting the presence of $\text{Fe}_2\text{O}_3$ within silt or clay fractions. The distribution of $\text{CaO}$ reveals a general decrease in the $\text{CaO}$ content contrary to that of $\text{SiO}_2$, $\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}$, $\text{K}_2\text{O}$, $\text{Fe}_2\text{O}_3$ along the section (Figure 2, Figure 3). This trend can be explained by alteration of carbonate units and units with greater clastic input. The distribution of $\text{MgO}$ reveals that there is no expressed trend for
distribution; this can be attributed to variations in the ecological and paleontological parameters of the environments under which the studied rocks were deposited. Therefore the ratio Ca/Mg values variate in wide range from 2.5 to 154 with average value 9.3 (Figure 4).

Chave [12] stated that the MgO content increases with salinity but is simultaneously affected by so many other factors that it cannot serve as an adequate indicator”. He also noted that in carbonate sediments the Ca/Mg ratio increases seawards with depth. Chilingar et al [13] stated that “in as much as shallow near-shore waters are systematically warmer as a rule than deep off-shore waters; the gross Ca/Mg ratio reflects temperature-depth-distance from shore”. The distribution of the Ca/Mg ratio values along the section (Figure 4) can be attributed, according to [14] to the selective adsorption of Mg \(^{2+}\) by illite clays besides the dolomite. The gross ratio reflects the illite content or perhaps the degree of diagenesis of the studied rocks.

The paper [15] stated that weathering means the approach to equilibrium of a system involving rocks, air and water, and the agents of chemical weathering namely moisture, free oxygen, carbon dioxide, organic acids and nitrogen acids. Krauskopf [15] suggested the following weathering index to compare

\[
\text{Weight } \% = \frac{\text{MgO}}{\text{CaO}} \times 100
\]
the degree of decay for a series of rocks, and since the weathered material loses Ca, Mg, Na and K and appears to gain Al and Fe, this fraction will obviously decrease:

Weathering index = (CaO + MgO + Na₂O + K₂O)/(SiO₂ + Al₂O₃ + Fe₂O₃ + CaO + MgO + Na₂O + K₂O)

The computed weathering index for the section is shown in Figure 2. The weathering index high values (near 1) for carbonate sediments suggest that the studied rocks are slightly affected by the agents of weathering. The low value is mostly due to dominate clastic materials rich in SiO₂, Al₂O₃, and Fe₂O₃. Consequently the abundance and distribution characteristics of the major components and trace elements reflect that occurring due to effect and nature of medium of deposition of the sediments.

Comparing geochemical variations (Figure 2) allows for defining silica and calcium as major elements to form geochemical zonation. Weathering index and SiO₂/Al₂O₃ ratio can be used as support proxy. An evaporate input in beds is expressed by S contents (weigh %) variations (Figure 2).

A clastic input is revealed in the beds 14, 15, 18, 21, 22, 23, 25, 29, 30. The greater evaporate input is mentioned in the beds 19, 21, 23, 30. The beds 1-13, 16, 17, 19, 20, 24, 26-28, 31 are predominantly composed of carbonate rocks (dolomarl and dolostone).

Geochemical classifications based on the Ca and Mg ratios [16] of the carbonate rocks could not be applied to our reference samples. Indeed, such an approach does not take into account the uncarbonated portion and depends on limits that are partially determined by the origin of the rocks. For example, Ca/Mg < 3.5 would imply a chemical precipitation of calcite or almost complete dolomite mineralization, whereas Ca/Mg > 105 would indicate either a chemical precipitation of calcite.

We used the developed construction of Martinet and Sougy's Diagram as a regular ternary diagram after [17] (Figure 5) where D, K and I are virtual contents of dolomite, calcite and insoluble residue (in particular, silica and silicate minerals) respectively in the analyzed samples. The final result of the regular ternary diagram application to our samples is shown on Figure 2.

Figure 5. The position of analyzed samples in the regular ternary diagram for classifying carbonate rocks from their weight percentage contents of calcite (%), dolomite (%) and residue (%) [17]- 1: dolomites; 2: siliceous dolomites; 3: dolomitic cherts; 4: calcareous dolomites (57 samples); 5: calcareous-siliceous dolomites (20 samples); 6: dolomitic-calcareous cherts (3 samples); 7: dolomitic limestones (31 samples); 8: dolomitic-siliceous limestones (2 samples); 9: calcareous-dolomitic cherts;
10: more or less magnesian limestones (4 samples); 11: more or less magnesian siliceous limestones (1 sample); 12: more or less magnesian calcareous cherts; 13: impure cherts; 14: cherts.

XRF data permit to upgrade the first version of Noinsky’s cycles [4] with new version of Noinsky’s cycles II (Figure 6).

| Number | Bed     |
|--------|---------|
|        | H       |
|        | 31      |
|        | 30      |
|        | 29      |
|        | G       |
|        | 28      |
|        | 27      |
|        | 26      |
|        | F       |
|        | 25      |
|        | 24      |
|        | 22      |
|        | E       |
|        | 21      |
|        | 20      |
|        | 19      |
|        | D       |
|        | 17      |
|        | C       |
|        | 16      |
|        | 15      |
|        | B       |
|        | 13      |
|        | 12      |
|        | 9       |
|        | A       |
|        | 5       |
|        | 2       |

**Figure 6.** The upgrading of Noinsky’s cycles scheme on XRF data. Each cycle composed of three facies components: marine (blue colored), evaporate (yellow colored) and terrestrial (green colored).

Secondary changes of carbonate rocks were tested by ratios Mn/Sr and Fe/Sr. “Good” samples are characterized by values of Mn/Sr<5 and Fe/Sr<20 for limestones and Mn/Sr<10 and Fe/Sr<60 for dolomites [18, 19]. Figure 7 demonstrates the distribution of these characteristic values. Values of Fe/Sr are reported as a decisive criteria to select “good” samples, which are likely to preserve isotope signature. The “bad” samples are at levels 29,25 m (bed 23); 30.2 m (bed 24); 32.7 m and 33.5 m (bed 25); 45.9 m and 47.25 m (bed 29); and 51.15 m (bed 30). The “good” samples can be considered as justified for $\delta^{13}C_{carb}$ and $^{87}Sr/^{86}Sr$ changes along the section (Figure 7).
Figure 7. The distribution of the values of Mn/Sr and Fe/Sr ratios in comparing with carbonate rocks types. Legends to lithological column see on the Figure 2.

Stable isotope geochemistry is considered as the most powerful method in chemostratigraphy. The oxygen isotope records provide most relevant information on the ice ages and reconstruction of marine environments on a global scale. The importance of stable carbon isotope geochemistry for paleoceanography and for stratigraphy was recognized in the mid-1970s [20].

The oxygen isotope composition of calcium carbonate is dependent on the isotopic composition of the ambient fluid and on the temperature of precipitation [21, 22]. Oxygen-isotope records from lithified sediments cannot be used confidently for high resolution oxygen isotope stratigraphy because of diagenesis. Only sediments which escaped deep-burial diagenesis can preserve oxygen isotope compositions which may be useful for some paleotemperature reconstructions (e.g. [23]).

While diagenesis increasingly alters the oxygen-isotopic signature of marine sediments, C-isotope geochemistry is less influences by diagenesis. The carriers of marine carbonate isotope signatures are either individual fossils or bulk carbonate (e.g. [24, 25].

In the Palaeozoic sections a much higher temporal resolution can be achieved by analysis of whole rock, preferentially micritic carbonates [20]. Although carbonates will recrystallize (dissolution of aragonite and high-magnesium calcite and reprecipitation of low-magnesium calcite) and be cemented during diagenesis, the initial carbon isotope ratios have a fair chance to be preserved as long as diagenesis proceeds in a system closed for carbon. Analyses of carbonates rich in organic carbon or embedded in organic carbon-rich shales may not provide reliable carbon isotope records due to the contribution of isotopically light carbon from the remineralization of organic carbon [20].
The section Pechishchi is predominantly composed of micritic carbonates but terrigenous component is also significant (Figure 2, Figure 6, Figure 7).

In [3] the data on Pechishchi were received for 14 samples. The mean value of the δ^{13}C_carb was 5‰ V-PDB. The new data on 28 samples are characterized by the mean value of the δ^{13}C_carb = 6.2 ‰ V-PDB. These values are close to each other (the values difference can be explained by a difference of sampling within the same beds). The negative excursions of δ^{13}C_carb are mainly associate in the section with clastic inputs (Figure 7): stronger land-derived inputs of freshwater [26, 27], remineralization of organic carbon to CO\textsubscript{2} forming bicarbonate in sea water [28], or a fluctuating sea level leading to a subaerial exposure of shallow water sediments and diagenetic overprinting [20, 29].

Strontium isotope stratigraphy is increasingly frequently used for estimating the duration of stratigraphic breaks and intervals and for identifying marine and non-marine depositional environments. 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 in 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. 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, i.e. as the Capitanian [29].

Age estimations and correlation of sediments using the ^{87}Sr/^{86}Sr ratio are based on its regular variations over geological time. On one hand, the comparison of measured ^{87}Sr/^{86}Sr ratios in marine carbonates with the Phanerozoic ^{87}Sr/^{86}Sr curve allows the study of the position of samples relative to this curve. On other hand, the ^{87}Sr/^{86}Sr ratio can be used for correlating sections.

Let us correlate the acquired ^{87}Sr/^{86}Sr data on the studied section with the Phanerozoic ^{87}Sr/^{86}Sr curve (Figure 8) [24].

The values of ^{87}Sr/^{86}Sr ratio in the massive of 17 justified definitions change from 0.707267 to 0.707417 (mean value 0.70734, standard deviation 0.00004) (yellow field (Figure 7, Figure 8)). Linear regression trend lies in band between 0.70736 (the bottom of the section) and 0.70727 (the top of the section) with width of band 0.0009. Most of the points belongs to marine components of cycles (beds of the Lower Kazanian substage top and beds 1-4, 6-8, 17, 26 of the Upper Kazanian substage – 12 points), less of the points relates to evaporate components (beds 9, 10, 19 of the Upper Kazanian substage – 3 points) and continental components of cycles (beds 24 and 30 – 2 points). Mean values of ^{87}Sr/^{86}Sr on marine component, evaporate component and continental component of Noinsky’s cycles equal 0.707344, 0.707321 and 0.707301 respectively, reflecting global ^{87}Sr/^{86}Sr change. The age of the Kazanian stage was estimated by the interval 270,6±0,7 Ma –265,8±0,7 Ma [30].

A decrease in the ^{87}Sr/^{86}Sr ratio, recorded for the Kazanian, generally corresponds to the global curve (Figure 8) and indicates the connection between sedimentation basins and the sea. On Phanerozoic ^{87}Sr/^{86}Sr curve observed values can be attributed to the interval 273 – 268 Ma (yellow field, Figure 7, Figure 8), and in the trend band – to the interval 270-268 Ma (green field, Figure 7, Figure 8) respectively.
5. Conclusions

New version of Noinsky’s cycles scheme has been obtained for Martinet and Sougy’s Diagram types of carbonates, with the geochemical indices values changing within the clastic beds 14, 15, 18, 21, 22, 23, 25, 29, 30; evaporate beds 19, 21, 23, 30 and carbonate beds 1-13, 16, 17, 19, 20, 24, 26-28, 31.

“Good” samples of carbonate rocks are characterized by the mean value of the $\delta^{13}$C$_{\text{carb}} = 6.2 \, \% \, V$-PDB. The negative excursions of $\delta^{13}$C$_{\text{carb}}$ values (with amplitudes 2-8 \%) are assigned as significant land-derived sedimentary inputs.

The values of $^{87}$Sr/$^{86}$Sr ratio in the data set of 17 justified definitions change from 0.707267 to 0.707417 (mean value 0.70734). On Phanerozoic $^{87}$Sr/$^{86}$Sr curve observed values attribute to the interval 273 – 268 Ma.

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