VOL. 12, NO. 21, NOVEMBER 2017 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

THE VARIATIONS OF THE $\delta^{13}C$ AND $\delta^{18}O$ IN THE MIDDLE PERMIAN ROCKS, VOLGA RIVER OUTCROPS, RUSSIA

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ABSTRACT

Data on stable isotopes of carbon and oxygen of the Permian carbonate rocks play an important role to create geochemical frame of the Permian formations. The stable isotopes records reflect changes in chemical composition of carbonate rocks in dependence on regional and global factors in history of the Permian period. Variations of stable isotopes across the Middle Permian rocks correlate with the stratigraphic boundaries and paleoenvironmental changes.

Keywords: the Permian rocks, sedimentary cycles, spectral analysis.

1. INTRODUCTION

The Permian sections relate to the key objects to recognize the Paleozoic history end when the supercontinent Pangea agglomerated, the sea level fell, massive volcanism occurred and mass extinction was triggered. During the Permian the continent Euroamerica was occupied by a lot of endemic sedimentary paleobasins under an arid climate.

In the present paper the Urzhumian stage rocks have been regarded. The Urzhumian stage forms the upper part of the Middle Permian series (regionally the Biarmian series) of the Permian system. The Urzhumian rocks are outcropped on Vyatka, Volga, Kama Rivers. These outcrops contain a lithologic and stratigraphic record of many interesting geological processes caused by paleoenvironmental factors.

According to previous C-isotopic and O-isotopic ratios data received from the carbonate Permian rocks of Volga-Kama region [1, 2] the values $\delta^{13}C$ decrease up the Urzhumian section to minimum -1 ‰ PDB and mean value of $\delta^{18}O$ in the section is 0.5 ‰ PDB. The significant increase of $^{87}Sr/^{86}Sr$ in bulk carbonates up the Biarmian section can be explained by the decreasing of open sea influence on depositional settings.

In this paper C-isotopic and O-isotopic data have been discussed in light of excursion boundaries search. These new data have been received from the two Volga river Urzhumian outcrops (Monastery ravine and Cheremushka ravine) and firstly presented in [3-6].

2. OBJECTS AND DATA DESCRIPTION

The Urzhumian stage at site Cheremushka begins from unconformity between Kazanian and Urzhumian Stages. It comprises lower (Sulitzkian) and upper (Isheevskian) suites. Lithology and fauna characteristics of these suites were given in [4, 7]. The boundary between suites is the bottom of green clays layer with the first occurrence of non-marine bivalves. This early Urzhumian association is represented by species *Palaeomutela algae* Gus., *Prilukiella* sp., *Anadontella volgensis* (Gus.) belonging to a set of guide fossils.

The Sulitzkian suite is composed of seven terrigenous and carbonate layers (layers 1-7 up the section) with rare fossils (fish flakes): 1) sandstone (quartz arenite): brown; fine grained; subangular; locally clayey-silty; thickness is 3.15 m; 2) marl: greenish and pinkish-grey; locally contained large dolomite crystals; horizontally and wave bedded; comprised of clay minerals palygorskite and montmorillonite; thickness is 2.05 m; 3) siltstone and claystone: brown; wave bedded with thin layers of sandstone: greenish-grey; fine-grained and marl: grey; contained rare fish flakes; thickness is 4.6 m; 4) dolomite and marl: grey; contained halite crystals; wave and horizontally bedded; included rare fish flakes; thickness is 5.05 m; 5) claystone and siltstone: brown; wave bedded; with rare thin layers of sandstone (quartz arenite): greenish-grey and brown; fine-grained; contained shells of conchostracans and fish flakes; thickness - 2.55 m; 6) alternation of marls: grey, pinkish, greenish, brown; wave and horizontally bedded with siltstones and claystones: red and brown; thickness is 5.85 m; 7) bottom part (2.9 m) is composed of sandstone (quartz arenite): grey and yellow; clayey carbonate cemented; locally included siltstone and sandstone: red and brown. Upper part (2.8 m) is represented by claystones and siltstones: brown, yellow and red. Top (0.65 m) is composed of marl (dolomite): grey; locally included claystone: red; thickness is 5.55 m.

The Isheevskian suite comprises of seven terrigenous and carbonate layers (layers 8-14 (Figure-1)) characterized by a number of fossils: 8) claystone: red, brown and green; wave bedded; with a number of thin layers of marl: yellow and brown, siltstones and sandstones: greenish-grey. Claystone and siltstone contain fossils of bivalves, ostracods, conchostracans, fish flakes and plant remains. Main clay mineral is montmorillonite. Green colored claystones that are in 1 m above bottom contain non-marine bivalves. Top and bottom parts include white marl; thickness is 7.3 m; 9) lower part is composed of dolomite: grey; cryptogenic; alternated with up marl dolomitic. Upper part contains limestones: grey; algal; included bivalves and ostracods. Dolomite, marl and limestone interspersed with thin layers of mottled claystones and siltstones; thickness - 6 m; 10) claystone: brown; horizontally bedded with thin layers of limestone,

sandstone and siltstone. In middle part of layer it is observed mottled band marl and limestone (thickness 1.7-2.7 m). Claystone and marl contain fossils of bivalves, ostracods and fish flakes; thickness is 6.65 m; 11) alteration of limestone: grey; algal and marl with mottled claystone and siltstone with bivalves and ostracods. Thickness is 6.6 m; 12) claystone: brown; horizontal bedded; contained fossils of bivalves, ostracods, conchostracans, fish flakes; alternated with up sandstone (thickness 2-3.25 m): grey and greenish-grey; cross-bedded, polymictic, with slightly rounded grains. Sandstone is overlapped by thin alteration (thickness 2-2.4 m) of marl, dolomite and claystone mottled; wavy bedded. Clay minerals are represented by montmorillonite-chlorite and montmorillonite-illite mixed phase, corrensite and palygorskite; thickness is 7.5 m; 13) limestone: grey; algal; massive; cavernous; in upper part contained siltstone: red; interbedded with thin layers of marl: colorful (pink, green, purple); with fossils of bivalves and ostracods. Top rocks in some areas deeply eroded. Clay minerals are represented by montmorillonite-chlorite and montmorillonite-illite mixed phase, corrensite and palygorskite; thickness is 6.6 m; 14) limestone, dolostone and marl; thickness is 6 m.

The Monastery Ravine is located on the right bank of the Volga River, in the vicinity of the villages of Monastyrskoye and Il'inskoe [3, 5, 6].

The Urzhumian stage includes three formations.

The lower formation I is composed of red-bed shales and distinctly subdivided into two parts. The shales of the lower part of the formation contain beds (3-20 cm thick) of grey and pink marls, rarely of brown siltstones and sandstones. In the upper part of the formation, shales are more homogenous and have a few beds of terrigenous and carbonate rocks. The shales often bear thin lenses of palygorskite.

Fossils occur rarely in the formation and mostly in its upper part. The first bed with fossils lies 10 m below the top of the formation and is composed of reddish-brown thinly bedded shales containing small (3-4 mm) distorted valves of conchostracans. Seven meters above this bed, dull-red imbedded shales, along with conchostracans, contain the isolated scales of the fishes *Platysomus biarmicus* Eichw., *Kargalichthys efremovi* Minich, *Amblypterina (Eurynotoides) costata* (Eichw.), *Acrolepis rhombifera* Eichw., *Palaeoniscum* cf. *kasanense* Gein. et Vetter, *Palaeoniscum* cf. *freislebeni* Bl., *Palaeoniscum kurtum* Krotov, *Varialepis orientalis* (Eichw.), *Varialepis bergi* A. Minich, *Elonichthys* sp., *Eurysomus* sp., and *Xenosynechodus* sp. The scales are 2-5 mm in size, black, not oriented and regularly distributed in the rock.

The formation II contains argillaceous-carbonate members. These members are separated by two members of sandy-argillaceous rocks. The argillaceous- carbonate members are composed of greenish and pinkish-grey argillaceous carbonate rocks (0.2-1.5 m thick), containing thin (usually10-30cm) bands of red shale. The sandy-argillaceous members are composed of reddish- brown shales and siltstones with lenticular beds of brownish sandstones (up to 2m).

Fossils are represented by non-marine ostracods, bivalves, fishes, amphibians, and plants. The bed of the greenish-grey siltstone (5-20 cm), 6.5 m above the base of the formation, contains numerous scales of the fishes *Platysomus biarmicus* Eichw., *Amblypterina (Eurynotoides) costata* (Eichw.), *Amblypterina (Eurynotoides)* sp., *Palaeoniscum* cf. *kasanense* Gein. et Vetter, *Palaeoniscum* sp., *Varialepis bergi* A. Minich, *Elonichthys* sp., *Eurysomus* sp., and *Xenosynechodus* sp. The large (0.5-3.0cm) reddish-brown scales occur parallel to the bedding planes and mainly concentrate in the thin (3-5 mm) bed, which also yields small amphibian bones.
Eight meters below the top of the formation, the bed (0.1 m) of reddish-brown evenly and thinly laminated shale contains molds of the ostracods *Palaeodarwinula* cf. *fragiliformis* (Kash.), the bivalves *Palaeomutela castor* (Eichw.), *P. doratioformis* (Gus.), *Prilukiella subovata* (Jones), scales of the fishes *Varialepis* cf. *orientalis* (Eichw.) *Platysomus*sp. ,*Elonichthys*sp., fragments of the small-leafed plant *Phylladoderma tscheremushca* Esaul., and the remains of *Paracalamites frigidus* Neub. and *Stomochara diserta* Kis.

The formation III is composed of reddish-brown shale and siltstones that are usually intercalated by thick lenses of yellowish-brown, obliquely laminated sandstones. Carbonate rocks are represented by grey, nodular, and muddy limestones and marls. Different levels within the formation contain the remains of non-marine bivalves, ostracods, conchostracans, fishes, and tetrapods, and imprints and fragments of plants. Grey and brown siltstones 1-1.5 m above the base of the formation contain coaly remains of the trunks of *Sphenophyllum stouckenbergii* (Schm.) and *Paracalamites frigidus* Neub.
In present paper we discuss the data on the stable isotopes of carbon and oxygen in the section in the Monastery ravine and in the Cheremushka section which were firstly presented in [3-6]. Measurements of isotopic composition were conducted on mass spectrometer DELTA in the laboratory of isotope Geochemistry and geochronology, Geological Institute (Moscow).

3. C-ISOTOPIC AND O-ISOTOPIC VARIATIONS

The variations of C and O isotopic ratios are shown on Figure-1. Changes $\delta^{13}C$ and $\delta^{18}O$ occur in the range of -8 to +4 ‰ PDB and -12-+4 ‰ PDB, respectively. The local minimums of the oxygen indicator correlate with layers 10, 12, 14 in the Cheremushka section; the carbonate packs II-4 and II-5 in the Monastery ravine. Local minimums of $\delta^{13}C$ correlate with the layers 8, 12, 14 in the Cheremushka section; the carbonate packs II-2, II-4 of the section in the Monastery ravine section.

Green line of the correlation (between the layer 10 and the carbonate pack II-4) is most expressive and can be interpreted as possible regional arid climate weakening. The identified line of the correlation separates the lower part of Urzhumian stage (the Sulitzkian suite + the lower part of the Isheevskian suite in the Cheremushka section and the formation I and lower part of the formation II in the Monastery ravine section), characterized by higher

values of the isotope records from the upper part (the remaining part of the Isheevskian suite in the Cheremushka section and the formation II in the Monastery ravine section), which is characterized by lower values of the isotopic ratios but with a more deviations around mean value.

The plot C-isotopic vs. O-isotopic data is shown on the Figure-2. It is observed a stratigraphic affiliation of the data in the cloud of points including also the Upper Kazanian data from [1, 2, 8].

Figure-3 and Figure-4 demonstrate the position of mean isotopic values for Volga-Kama rivers region using discussed data and data from [1, 2, 8] in the cloud of points and the relatively smooth curve from [9].

Figure-3 shows that the samples from the Asselian, the Sakmarian and the Kazanian belong to the cloud or nearly with it. The samples from essentially continental sediments (the Ufimian stage, the Urzhumian stage and the Tatarian series) are found far from the cloud (regional and facial effect or bulk analysis effect).

Only the samples of the Kazanian age are located close to the curve on the Figure-4. The samples from the Urzhumian stage and from the Tatarian series are found within the cloud. The samples from the Lower Permian and Carboniferous are located far from the cloud due to regional or bulk analysis effects.

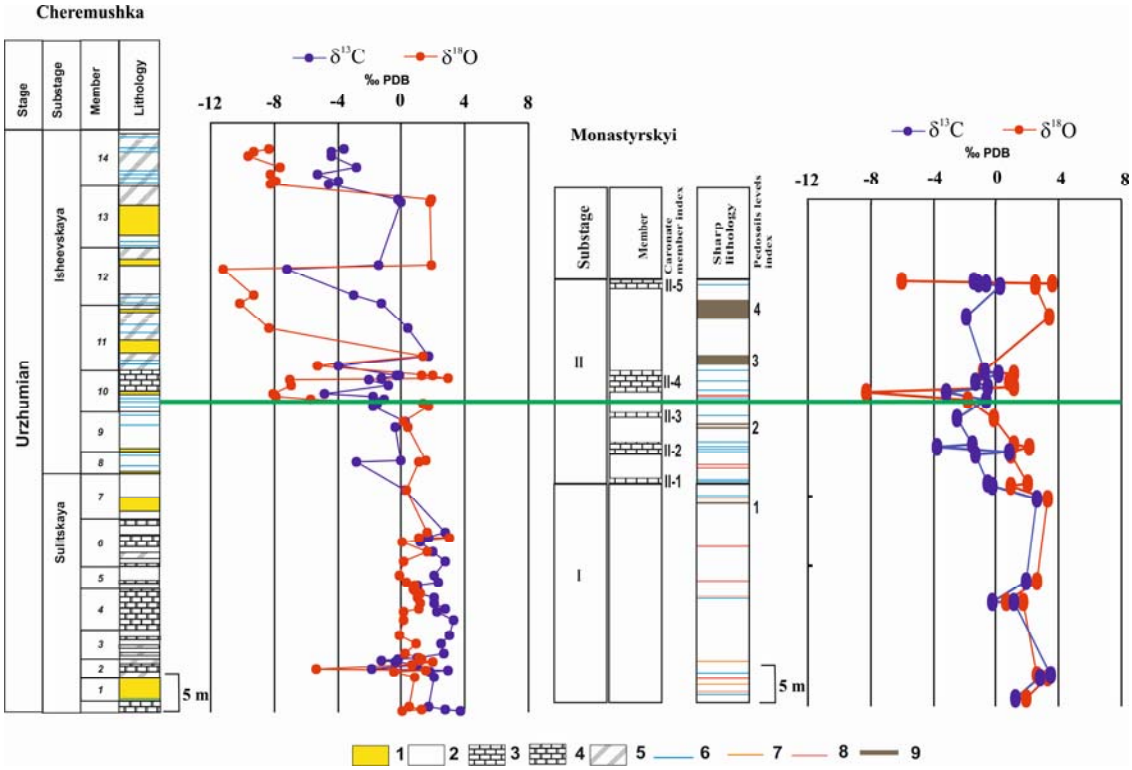

Figure-1. Variations of stable isotopes of carbon and oxygen in carbonate rocks. In the Cheremushka section the layers are marked with italic numbers. In the Monastery ravine section (Monastyrski) the formations I and II (substages) are shown. Legends: 1 - sandstones, 2 - claystones, 3 - limestones, 4 - dolomites, 5 - marls, 6 - carbonate level, 7 - palygorskite, 8 - breccia levels, 9 - paleosoil level.

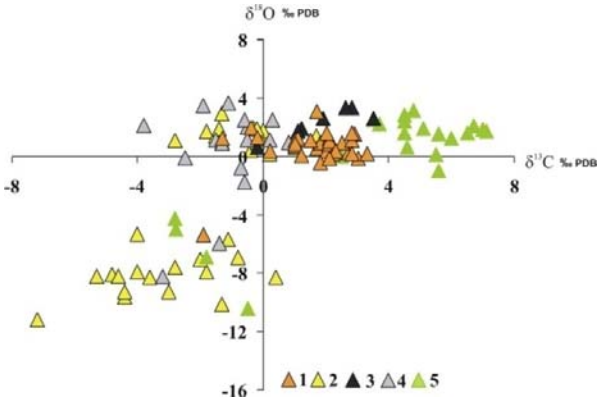

Figure-2. C- isotopic values vs. O-isotopic values plot. Legend: 1 - the Sulitzkian suite in the Cheremushka section; 2 - the Isheevskian suite in the Cheremushka section; 3 - formation I in the Monastery ravine section; 4 - formation II in the Monastery ravine section; 5 - the Upper Kazanian.

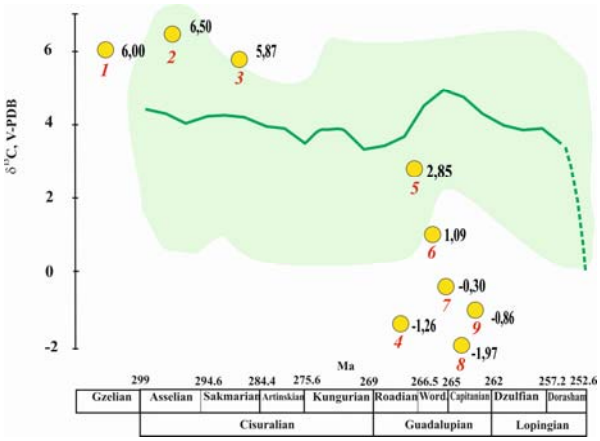

Figure-3. The position of regional data on plot after [Korte *et al*, 2005], including a cloud of points (brachiopods data) and the smoothed valid curve (in green). Yellow circle indicate regional data on samples from the following stratigraphic units: 1 - the Upper Carboniferous series, 2 - the Asselian stage, 3 - the Sakmarian stage, 4 - the Ufimian stage, 5 - the Lower Kazanian substage, 6 – the Upper Kazanian substage, 7- the Urzhumian stage, 8 – the formation III (the Tatarian series), 9 – the formation IV (the Tatarian series).

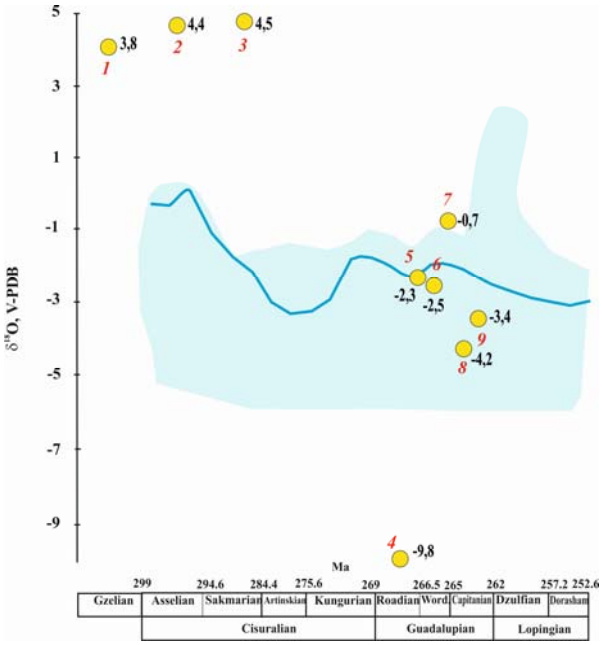

Figure-4. The position of regional data on plot after [Korte *et al*, 2005], including a cloud of points (brachiopods data) and the smoothed valid curve (in blue). Yellow circle indicate regional data on samples from the following stratigraphic units: 1 - the Upper Carboniferous series, 2 - the Asselian stage, 3 - the Sakmarian stage, 4 - the Ufimian stage, 5 - the Lower Kazanian substage, 6 - the Upper Kazanian substage, 7 - the Urzhumian stage, 8 - the formation III (the Tatarian series), 9 - the formation IV (the Tatarian series).

4. CONCLUSIONS

The C-isotopic and O-isotopic variations in the Urzhumian stage section reveal the expressive change corresponding to the layer 10 in the Cheremushka section and the carbonate pack II-4 in Monastery ravine section. The bulk data and shell data are close for the Kazanian rocks. Remaining data can be result of significant regional evolutionary deviations and bulk analysis data features.

ACKNOWLEDGEMENTS

This work was funded by the subsidy allocated to Kazan Federal University for the state assignment #5.2192.2017/4.6 in the sphere of scientific activities.

The financial support of the RFBR scientific research projects under 16-05-00706 project number is also gratefully acknowledged.

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