VOL. 11, NO. 23, DECEMBER 2016 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

THE LOWER KAZANIAN ROCKS AS SHALLOW MARINE FACIES (SOUTH-EASTERN TATARSTAN) ON GEOCHEMISTRY DATA

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ABSTRACT

The Middle Permian rocks (the Lower Kazaniansubstage, South-Eastern Tatarstan, reference section), were geochemically examined by XRF, ESR and isotope analysis to reveal chemostratigraphic frame of the Lower Kazanian substage. Facial changes and climate episodes were proposed on major and trace elements, ESR labels and isotope ratios relationship.

Keywords: the lower Kazaniansubstage, geochemistry.

1. INTRODUCTION

Basin of the Volga and Kama rivers is known as an unique stratigraphic and paleogeographic object formed in littoral, transition and continental environments. We considered the Kazanian stage (~ 272 - 266 million years) within the Late regional cycle [1]. The Late regional cycle can be characterized as a cycle of second order corresponding to the supercycle or sequence that began his formation after the fifth global regressive phase of the Late Paleozoic. At the beginning of the formation of the Upper regional cyclotheme most of the East European platform was a geological structure created by paleotectonic processes of the Middle Carboniferous – the Early Permian due to tectonic movements of the early Hercynian [2].

Hercynian Ural mountain structures were actively destroyed, and the eastern marginal area of the Russian plate was providing by a huge amount of clastic and chemogene sedimentary material. Western boundaries of these formations are traced by marginal uplifts system of Tokmovsky vault. Waters of Boreal Permian sea penetrated from north to Cisuralian foreland basin. Investigated Permian cycle acts as a foreland basin supercycle history from its opening until closing. Three megacycles corresponding to the Ufimian, Kazanian and Urzhumian+Severodvinskian + Vyatskian occurred inside this supercycle [1].

According to lithofacies zonation proposed in [3] the Kazanian rocks of Volga - Kama rivers area belong to the zone of carbonate marine and lagoon sediments.

The most interesting Permian sections in the South-Eastern Tatarstan (Volga-Kama rivers region) are exposed in the upper reaches of the Sheshma River, near the villages of Shugurovo and Karkali.

The Ufimian-Kazanian succession near the villages of Shugurovo and Karkali is well-known to Russian geologists and was studied for over 200 years [4]. Originally, the section attracted attention due to common occurrences of bitumen on the surface in the basin of the Sheshma River. In the north-eastern vicinity of the village of Shugurovo, outcrops of tar sandstone form a large field of heavy and viscous oil. This field was well-known since the 19th century and until recently was utilished by the Shugurovo Tar Plant. In 2015, the Shugurovo Tar Plant was transformed into the Memorial Park of Geological Heritage.

The present paper shows the geochemical observation of the sections near the village Karkali that indicates that the Lower Kazanian marine rocks can be represented as specific facial succession.

2. OBJECT

On the right slope of the valley of the Sheshma River, between the villages of Shugurovo and Karkali, the Ufimian red-bed rocks are overlain by the lowermost Kazanian beds composed of dark-grey, bituminous sandstones. The Lower Kazanian succession in this area is similar to the stratotypeKazanian sections in the Samara region, in the basin of the Sok River [4].

Several outcrops (A1-A5) were used to compile general profile of the section. Upwards in the section, the sequence in the right slope of the Sheshma River shows the following beds (from bottom to top) [4] (Figure-1).

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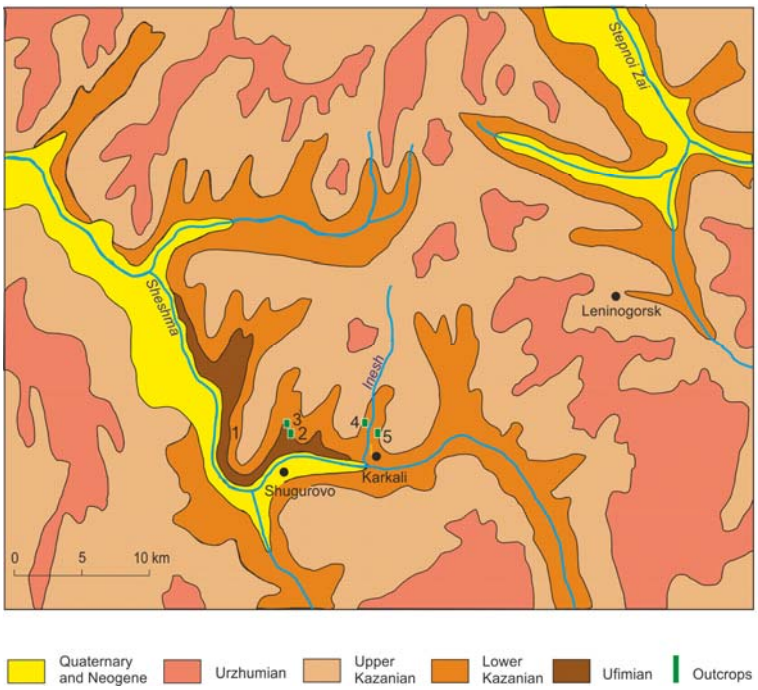

Figure-1. Map of probed sections. 1-5 – outcrops A1-A5.

Ufimianstage.Sheshmian formation (Horizon)

Bed A1/1 Interval 0.0–5.0 m Thickness (visible) 5.0 m

Sandstone: brownish-red, polymict, calcareous-muddy, fine-grained and medium-grained, cross-bedded or with disorderly structure, solid. Clastic grains: effusive rocks (50 %), quartz (35 %), feldspar (10 %), and sporadic flakes of biotite. Most grains are coated with a film of iron hydroxides. The upper surface of the Bed is eroded and slightly undulated. Horizontally, 300 m west of this station, the sandstone is replaced with variegated silty-argillaceous succession containing subordinate interbeds of light-grey, algal-microbial limestones. Laminated brownish-red shales contain rare non-marine bivalves *Palaeomutela*ex gr. *attenuata*Gus.,*P. (Palaeanodonta) castor* (Eichw.), and ostracods *Paleodarwinula*sp.

Shugurovo sandstone (Shugurovo beds)

Bed A1/2 Interval 0.5-7.0 m Thickness 2.0 m

Sandstone: from brownish greenish-grey in the lower part to light greenish-grey in the upper part; fine-grained (0.1-0.25 mm), polymictic, cross-bedded, solid. Clastic grains: quartz (50 %), effusive rocks (35 %), feldspar (10 %), and sporadic flakes of biotite. Quartz grains are slightly corroded, isometric, angular and subrounded. Uppermost part of the Bed (0.1 m) is represented by lightgrey calcareous solid sandstone textured by branching fissures of desiccation.

Bed A1/3 Interval 7.0–7.10 m Thickness 0.1 m

Limestone: pinkish-grey, grey, fine-grained, solid, with numerous small branched columns resembled micro-stromatolites. The columns are filled by sessile foraminifers *Tolypammina*sp. The bed top is uneven (due to the rounded upper surfaces of the columns) and contains rare marine bivalves *Netschajewia*sp. Horizontally, the quantity of branched columns is changed from abundant to sparse.

The Kazanian age of Shugurovo Sandstone is determined by conventions of the Interdepartmental Stratigraphic Committee of Russia basing on lithological and sequence-stratigraphical data. In the Karkali section, biostratigraphic boundary of the Kazanian is located above at the base of Bed A1/4 and defined by the first occurrence of the age-diagnostic conodont *Kamagnathus*[4].

Kazanian stage

Lower Kazaniansubstage

Baitugan beds

Lingula Shale member

Bed A1/4 Interval 7.10-7.45 m Thickness 0.35 m

Shale: greenish-grey, calcareous, soft, flexible, with numerous (up to 40 % of bulk rock) well preserved shells of brachiopods *Dielasmanetschajewi*Grig.,*Campbellelasmavariiforme*Smirn., *Campbellelasma vulgaris* Smirn., and fragments of branched bryozoans.

Bed A1/5 Interval 7.45–7.50 m Thickness 0.05 m

Limestone: grey and dark-grey with slight reddish and greenish tints, fine-grained, solid. The top surface is uneven which is caused by the shells of Dielasmatidae*in situ* (hence the name 'Dielasmovyiizvestnyak' – 'Dielasma Limestone') and small algal-microbial mounds. Foraminiferal assemblage: *Tolypammina*sp. (sessile forms),

Pseudoammodiscusmegasphaericus(Gerke), *Nodosaria*sp. Ostracods: *Healdia*sp., *Healdianella*sp., *Cavellina*sp., etc. Gastropods: *Goniasma*sp., *Loxonema*sp. Brachiopods: *Cleiothyridinapectinifera*(Sow.), *Dielasmanetschajewi*Grig.,*Campbellelasmavariiforme*Smirn., *Campbellelasma vulgaris* Smirn., and fragments of branched bryozoans. The number of bioclasts significantly decreases from the base to the bed top.

Bed A1/6 Interval 7.5-20.5 m Thickness 13.0 m

Shale: grey and dark-grey with slight greenish and yellowish tints, thinly bedded, platy. Thin interbeds (5 cm) of concretionary limestones and marls occur at the different levels. From the bottom to top, the lamination changes from thinly to medium and thick bedded. Some bedding planes contain assemblages of marine ostracods, inarticulate the brachiopods *Lingulaorientalis*Gol., the bivalves *Pseudobakewelliaceratophagaeformis*Noin., *Netschajewia*sp., branched and fenestrated bryozoans, and charred plant debris. The lowermost part of the Bed contains the brachiopods *Licharewiarugulata*(Kut.) and the conodonts *Kamagnathuskhalimbadzhae*Chern., the index-species defining the biostratigraphic boundary of the Kazanian Stage.

The overlying succession is more conveniently observed in outcrop A2.

Spiny Limestone Member

Bed A2/7 Interval 20.5-21.5 m Thickness 1.0 m

Limestone: yellowish-grey, bioclastic, coquina, medium-bedded, with numerous small foraminifers, ostracods, gastropods, brachiopods *Cancrinellacancrini*(Vern.), *Dielasmanetschajewi*Grig., *Licharewiarugulata*(Kut.), In some places the rock is overwhelmed by brachiopod spines (hence the name 'Spiny Limestone').

The base of the bioclastic limestone bed has the feeding burrows (10-15 mm in diameter) branched in the horizontal plane and filled with shell debris.

Bed A2/8 Interval 21.5-33.2 m Thickness 11.7 m

Alternation of yellowish-grey, medium-bedded marls, limestones and mudstones:several bedding planes contain pavements of the brachiopods *Cancrinellacancrini*(Vern.). The rock also contains ostracods, bivalves of *Nuculana*, *Lithophaga, Pseudobakewellia, Palaeolima*, the brachiopods *Licharewiarugulata*(Kut.), and *Dielasmanetschajewi*Grig. Some bedding planes contain only charred plant fragments with rare *Lingula*, as well as other ones contain only subhorizontal trace fossils and plant debris.

Spiny Limestone member

Bed A3/8 Interval 23.2-33.2 m Thickness (visible) 10.0 m

Alternation of yellowish-grey marls, limestones and mudstones; analogue of Bed A2/8.

Kamyshla beds

Bed A3/9 Interval 33.2–38.9 m Thickness 5.7 m

Sandstone: alternation of soft argillaceous and solid calcareous beds. Both types of sandstones are brownish and yellowish-grey, platy (1-20 cm), fine grained. Argillaceous sandstone contains charred plant debris that marks thin lamination. Some bedding planes contain the pavements of *Cancrinellacancrini*(Vern.). Usually rocks lack fossils.

Bed A3/10 Interval 38.9-40.7 m Thickness 1.8 m

Rhythmic alternation of sandstones and marls. Sandstone: grey, calcareous, solid, with fragments of brachiopod shells. Marl: light-grey, soft; some interbeds with abundant plant remains (including algae) and charred plant debris; some interbeds contain numerous juvenile brachiopods and bivalves. The bedding planes of sandstones are textured by ripples.

Bed A3/11 Interval 40.7-43.7 m Thickness 3.0 m

Sandstone:grey, yellowish-grey and brownish-grey, fine-grained, solid, with lenticular and crossbedded lamination, and flat pebbles of carbonate rocks at the base. Five levels with thin (2–10 cm) lenses of bioclastic and pelloidal limestone occur at the lower part of the Bed. Rocks contain fragments and debris of brachiopod shells. Thick solid plates of sandstone form rocky exposures on the slope. The lower surface of the Bed is eroded and slightly undulated.

Bed A3/12 Interval 43.7–45.2 m Thickness 1.5 m

Alternation of soft sandstone and limestone. Sandstone: yellowish-grey, calcareous, relatively soft.

Limestone: light-grey and yellowish-grey; argillaceous and arenaceous, soft, pelloidal and oolitic, bioclastic (brachiopods) and bioturbated, cavernous. Rocks contain fragments and debris of brachiopod shells and bryozoans.

Bed A3/13 Interval 45.2-46.7 m Thickness (visible) 1.5 m

Limestone: light-grey and yellowish-grey, oolitic, with bioclastic (brachiopods) lenses, with crossbedded lamination in the upper part. Bed forms the rocky exposures in the heads of the gullies. The full thickness of Bed 13 and overlying succession are observed in outcrop A5.

Bed A5/13 Interval 45.2–48.5 m Thickness 3.3 m

Limestone: light-grey and yellowish-grey, oolitic, massive, solid, with lenticular and cross-bedded lamination in the upper part. The lenses of bioclastic limestone contain internal moulds of bivalves and define lamination. Bed A5/13 represents first productive interval of the Karkali Limestone Quarry.

Bed A5/14 Interval 48.5–49.5 m Thickness 1.0 m

Limestone: light-grey and yellowish-grey, arenaceous or argillaceous, bioturbated, platy, with thin lenses of oolitic and bioclastic limestone. The latter contains the bivalves *Nuculanakasanensis*(Vern.), *Schizodusrossicus*Vern.,*Permophorus simplex* (Keys.), *Pseudomonotis (Trematiconcha) noinskyi*(Lich.), the brachiopods *Cancrinellacancrini*(Vern.), *Dielasmanetschajewi*Grig., fragments of bryozoans and crinoids. The overlying succession is observed in the east wall of the Karkali Limestone Quarry.

KrasnyiYar beds

Bed A5/15 Interval 49.5-50.2 m Thickness 0.7 m

Sandstone: greenish-grey and brownish-grey ('tobacco'), fine-grained, polymictic, calcareous and solid

in the lower part (0.4 m), argillaceous, thin laminated and soft in the upper part (0.3 m). Thin plates (approx. 0.5-1 cm) define lenticular lamination. The bedding planes contain rare fragments of brachiopod shells and charred plant debris.

Bed A5/16 Interval 50.2-52.9 m Thickness 2.7 m

Limestone: light-grey, grey, grey with slight brownish tint, oolitic, pelloidal, arenaceous, massive, with subordinate lenses of yellowish-grey marls. Several intervals of limestone are riddled with numerous upright channels (10-15 mm in diameter and up to 20 cm in height). The Bed can be divided into four parts, from base to top:

Bed A5/16-1 [0.00-0.25] Interval 50.2-50.45 m Thickness 0.25 m

Succession of yellowish-grey sandstone, limestone and marl. Thin interbed of calcareous sandstone with the pebbles and shell debris forms the basement of the bed. Overlying soft marl contains only charred plant debris. The upper part of the bed includes the plates of pelloidal and arenaceous limestone with abundant small shells of molluscs and brachiopods. Randomly oriented bioclasts indicate bioturbation. Bioclastic pavements are locally preserved in the upper part of the bed.

Bed A5/16-2 [0.25–1.55] Interval 50.45–51.75 m Thickness 1.3 m

Limestone: light-grey with slight brownish tint, oolitic, with numerous bivalves *Netschajewia*dispersed over the entire interval. The top of this subunit is slightly undulating, erosional. The top surface is penetrated with numerous upright channels (10-15 mm in diameter and up to 20 cm in height) resembling *Thallassinoides*.

Bed A5/16-3 [1.55–2.50] Interval 51.75-52.70 m Thickness 0.95 m

Limestone: light-grey, arenaceous, with the pebbles of carbonate rocks in the bottom and abundant upright channels over the entire interval. The upper part of the limestone becomes more arenaceous and contains the shell (bivalves) pavements.

Bed A5/16-4 [2.50–2.70] Interval 52.70–52.90 m Thickness 0.20 m

Shell coquina: light-grey and yellowish-grey, formed by internal moulds of the large schizodont bivalves *Oriocrassatellaplana*Golowk. The top of the bed is slightly undulating, erosional.

Horizontally, 10-30 m west of this station, bed A5/16-4 cuts off the underlying limestones up to the bottom of Bed A5/16. At this place, coquina is replaced with arenaceous cross-bedded limestone.

Further to the west, arenaceous cross-bedded limestone is replaced again with oolitic limestone with '*Thallassinoides'*.

Bed A5/17 Interval 52.9-53.6 m Thickness 0.7 m

Sandstone: grey-brown, in the upper part yellowish-brown, polymictic with mudstone beds (to 1 cm).

The lower part of the Bed (10 cm) is more argillaceous and contains abundant subhorizontal branched trace fossils (approx. 5-8 mm in diameter) and the numerous brachiopod shells *Cancrinellacancrini*Vern. The upper part contains the pavements of *Cancrinella*and rare shells of the Kazanian index-fossil *Licharewiarugulata*(Kut.).

Bed A5/18 Interval 53.6-57.6 m Thickness 4.0 m

Alternation of marls and subordinate interbeds of shale and sandstone. Marls: greenish-grey, soft, fine laminated, with the scyphozoan cnidarians *Conulariahollebeni*Gein., the bivalves *Lithophagaconsobrina*(Eichw.), the brachiopods *Dielasmanetschajewi*Grig., and *Cancrinellacancrini*(Vern.).

Shale: dark-grey with greenish-grey tint, calcareous, fine lenticular laminated platy, with charred plant debris and rare trace fossils.

Bed A5/19 Interval 57.6-60.6 m Thickness 3.0 m

Alternation of sandstone and marl. Sandstone: brownish-yellow, polymictic, fine-grained, with subhorizontal lenticular lamination. Marl: yellowish-grey, silty, with numerous pavements of bivalve shells and upright borrows resembling *Scolithos.* The pavements and trace fossils define the boundaries with adjacent sandstone beds. The shells of *Cancrinella*normally oriented to the bedding planes of marl indicate bioturbation.

Bed A5/20 Interval 60.6–60.85 m Thickness 0.25 m

Sandstone: greenish-grey, greenish-brown, fine-grained, polymictic.

Bed A5/21 Interval 60.85–61.45 m Thickness 0.60 m

Deepening-upward succession of yellowish-grey calcareous sandstone containing the lenses of marl and limestone. Large (up to 15 cm) pebbles of light-grey limestones with marine Kazanian bivalves in the lower part.

Bed A5/22 Interval 61.45–63.70 m Thickness 2.25 m

Sandstone: grey, fine grained, polymictic, lenticular laminated. Two equal beds of sandstone are divided by thin (0.15 m) interbed of calcareous mudstone. Mudstone contains brachiopods *Cancrinella,* bivalves and charred plant debris.

Upper Kazaniansubstage

Bed A5/23 Interval 63.70–63.90 m Thickness 0.20 m

Limestone: light-grey, fine-grained, arenaceous, locally preserving subhorizontal wavy lamination.

Horizontally, 200 m north of this station, in outcrop A7, the Bed is replaced with alternation of platy limestones and sandstones which thickness is increased to 1.5 m.

Bed A5/24 Interval 63.90–65.55 m Thickness 1.65 m

Limestone: light-grey, yellowish-grey, with oolitic and bioclasticinterbeds.The Bed can be divided into four parts, from base to top:

Bed A5/24-1 [0.00–0.60] Interval 63.90–64.50 m Thickness 0.60 m

Limestone: porous, oolitic and bioclastic, with solid laminated interbed in the bottom and abundant upright channels (two intervals, in 0.05-0.15 and 0.40–0.60 m from the base). Some channels are branched in their lower end. The rock contains dispersed internal moulds of gastropods and the large schizodont bivalves

*Oriocrassatellaplana*Golowk. The top of the bed is undulating, erosional.

Bed A5/24-2 [0.60–0.90] Interval 64.50–64.80 m. Thickness 0.30 m

Limestone: porous, bioclastic and riddled by upright channels in the lower part (0.0–0.2 m); arenaceous and horizontally laminated in the upper part (0.2-0.3 m).

Bed A5/24-3 [0.90–1.20] Interval 64.80–64.95 m Thickness 0.15 m

Limestone:bioclastic, platy, solid; bioclasts and plant debris define the fine horizontal lamination.

Bed A5/24-4 [1.20–0.90] Interval 64.95–65.55 m Thickness 0.60 m

Limestone:bioclastic, oolitic, bioturbated, with several types of upright slightly curved channels resembling *Scolithos*. Small bivalves *Schizodus*and *Netschajewia*are preserved probably *in situ*.

Bed A5/25 Interval 65.55–68.55 m Thickness 3.0 m

Alternation of sandstone, siltstone and mudstone: dark greenish-grey in the lower part and brownish-grey in the upper part. No fossils.

Summary section is shown on Figure-2.

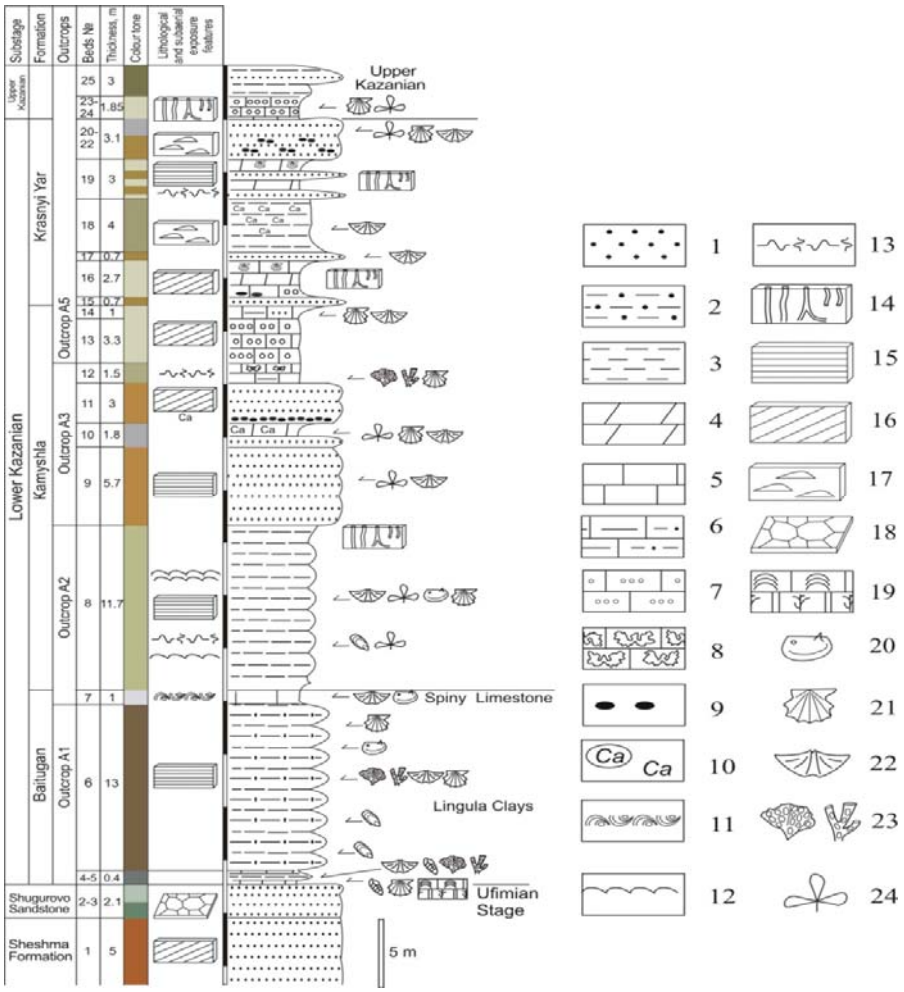

Figure-2. Summary section after [4]. Legends: 1 - sands and sandstones; 2- silts and siltstones; 3- shales argillaceous; 4- marls; 5- carbonate rocks; 6- argillaceous and silt carbonate rocks; 7-oolites; 8-vuggy carbonate rocks; 9-gravel, pebbles; 10 - calcareous concretions and calcareous recrystallization; 11- coquina; 12- shell pavement; 13-bioturbated structure; 14 - trace fossils; 15- horizontal and subhorizontal lamination; 16- cross lamination; 17- short lenticular lamination; 18- fissures of desiccation; 19- stromatolites and calcareous algae; 20- marine ostracods; 21- marine bivalves; 22- articulated brachiopods; 23- bryozoans; 24- leaves of higher plants.

3. GEOCHEMISTRY DATA: RESULTS AND DISCUSSIONS

Geochemical data were obtained by X-ray fluorescence (XRF) by methodics described in [5]; electron spin resonance (ESR) [4, 6], and stable isotope methods. Isotope composition was measured by Thermoelectron equipment including mass-spectrometer Delta V Advantage and Gas-Bench-II. Precipitation of probes and standards C-O-1 and NBS-19 was made in H_3PO_4 on temperature 50°C. $\delta^{13}C$ wasdeterminedin (‰) onV-PDBstandard. $\delta^{18}O$ was determined in (‰) on V-

SMOW standards. Accuracy of $\delta^{18}O$и$\delta^{13}C$ detection was ±0.2‰.

The distribution of samples as types of carbonate rocks was shown on Figure-3 after [7].

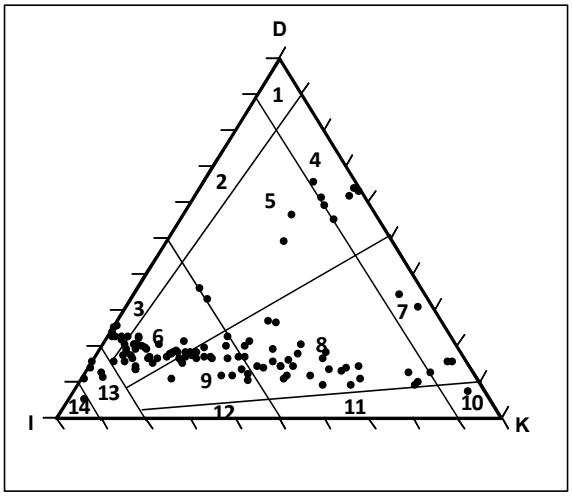

Figure-3. Regular ternary DKI diagram for classifying carbonate rocks from their weight percentage contents of calcite (%) (K), dolomite (%) (D) and residue (%) (I), after [7]. 1: dolomites; 2: siliceous dolomites; 3: dolomitic cherts; 4: calcareous dolomites; 5: calcareous-siliceous dolomites; 6: dolomitic-calcareous cherts; 7: dolomitic limestones; 8: dolomitic-siliceous limestones; 9: calcareous-dolomitic cherts; 10: more or less magnesian limestones; 11: more or less magnesian siliceous limestones; 12: more or less magnesian calcareous cherts; 13: impure cherts; 14: cherts.

Most of samples lie in areas 6, 8, 9 (dolomitic-calcareous cherts; dolomitic-siliceous limestones, calcareous-dolomitic cherts).

The position of samples along the section was shown on DKI zones on Figure-4 with XRF, ESR and isotope data. Characteristics of environments were shown in Table-1 after [4] with additions.

The dominant calcite mineralization was fixed at the lower part of the section (beds 4-9) on Mn^{2+} labels.

The dolomite mineralization (on α label) was observed at the upper part of the section (beds 10-13, 16, 18, 21–24). The bottom of bed 10 was revealed as the low level of dolomite mineralization zone.10-13, 16, 18, 21-24). The bottom of bed 10 was revealed as the low level of dolomite mineralization zone.

The paramagnetic labels SO_3^-, PO_2^-, C_{600} point on unaltered carbonates, especially, in beds 10, 12, 16, 18. The labels of E'-centres and R-centres reflect events of terrestrial flux, especially, during KrasnyiYar time. Beds 23-24 (the Upper Kazanian) are composed of significantly altered carbonates (on the absence of labels SO3-).

On XRF data, three components are revealed as the most important. There is silicon (quartz), calcium (carbonate minerals) and aluminum (argillaceous minerals) in the composition of investigated rocks. On the summary section, one can see that the sum of these elements is greater than 70 %. A marine paleobioproductivity and paleoredox-conditions can be interpreted in Cu, Ni, Zn and Mo variations, respectively [8].

The geochemical variations specifically reflect the lithostratigraphic and the facial alternation within the Lower Kazanian succession (Figure-4; Table-1) [4, 6]. Isotope data (Table-2) essentially deepen geochemical and facial framework (Figure-4).

VOL. 11, NO. 23, DECEMBER 2016 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

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Table-1.

Stratigraphic unit	Beds no.	Sedimentary environments	Sealevel, a.u.	DKI zone (Figure-3)	Paramagnetic labels	XRF labels
Ufimian stage	1-3	Delta	I	6,7,13,14	-	Redox-potential is not high
Baitugan beds	4-5	Littoral	III	6, 7	Mn^{2+},SO_3^-, E'	Redox-potential is low
	6	Transgression. Sublittoral. Below base of waves.	V	3, 6	Mn^{2+}, SO_3^-	Bioproductivity is high.
	7	Shallowwater. Littoral	III	6	Mn^{2+}, SO_3^-	Redox-potential is low
Kamyshla beds	8	Regression. Shallowwater. Littoral	II	6, 8, 9 (most of cases), 7, 10, 13 (single cases)	Mn^{2+}, SO_3^-	Bioproductivity is not high, redox-potential is not high
	9-11	Passive shallow water. Channels and ichnofossils	III - IV	4, 6. 7, 9	Mn^{2+}, SO_3^-, E'	Bioproductivity is high, redox-potential is not high
	12	Local transgression. Littoral.	V	9	Mn^{2+},SO_3^-, SO_2^-, C_{600}, PO_2^-	Redox-potential is low Bioproductivity is decreasing
	13	Ooiltes. Littoral	IV	9	Mn^{2+},SO_3^-, C_{600}	Bioproductivity is high
	14	Oolitesandichno fossils. Littoral.	III	6, 8, 9	Mn^{2+},SO_3^-, C_{600}	Bioproductivity is high, redox-potential is not high
KrasnyiYar beds	15	Active littoral	III	9	Mn^{2+}, E', R, PO_2^-	Redox-potential is high
	16	Local lagoons	II	5	Mn^{2+}, SO_3^-, C_{600}	Bioproductivity is high, redox-potential is high
	17	Channels	II	8		
	18	Active littoral	II-III	4, 6	Mn^{2+}, E', R, PO_2^-, SO_3^-, SO_2^-	Redox-potential is high
	19	Littoral	III-II	4, 6		Redox-potential is high
	20-22	Littoral with channels	III		Mn^{2+}, E', R, C_{600}	Bioproductivity is high, redox-potential is high
The Upper Kazanianssubstage	23-24	Oolitesandichno fossils. Littoral	III	4, 5, 7	Mn^{2+},SO_3^-, SO_2^-, PO_2^-, C_{600}, C_{350},E', R	Bioproductivity is high
	25	Littoral with channels and fans	II	9	-	Redox-potential is not high Bioproductivity is high

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Table-2.

Sample	Bed	Level up the section, m	$\delta^{13}C$, ‰ V-PDB	$\delta^{18}O$,‰ SMOW
17	4	7,2	-5,1	23,3
20	5	7,5	-5,1	22,4
27	6	11	-11,8	24,6
34	6	14,5	-1,8	21
42	6	19	-1,9	21,2
52	8	24,4	1	22,9
69	8	29,8	0,7	24
72	8	30,8	2,5	25,9
101	10	40,5	1,7	33
109	12	45,2	-3,5	29,7
111	13	46,5	2,8	21,4
114	13	48,5	3,5	22,9
129	16	51,3	2,5	23,5
136	16	52	2,2	22,8
147	18	56,5	3,4	33
149	19	60,6	2,8	32,5
156	22	62,8	1,2	28,4
157	22	63,1	2	30,4
160	24	63,9	2,8	31,1
165	24	64,9	-3,5	32,2
		minimum	-11,8	21
		maximum	3,5	33
		mean	-0,18	26,3
		st.dev.	3,95	4,4
		number	20	20

Received values belong to the range of values specific to the Lower Kazanian rocks of the Volga-Kama basin [9].

One can see on Figure-4 that the zones A, B can be interpreted as climate cooling episodes (increase of $\delta^{18}O$ because of lower water temperature and reducing the energy of the motion of “heavy” molecules). Zone C corresponds to a relative climate warming (decrease of$\delta^{18}O$; increase of biological productivity and concentration of carbon dioxide), D- evaporate episode (high mobility of the "heavy" oxygen and low biological productivity).

From the stratigraphic point of view, a sharp change in the behavior of the isotopic ratios is noted in the bottom of bed 13 (the top of Kamyshla beds). Baitugan and most of Kamyshla time can be characterized as cold episodes. Then the climate trend changed to warm and even evaporate conditions (dolomitization) [10].

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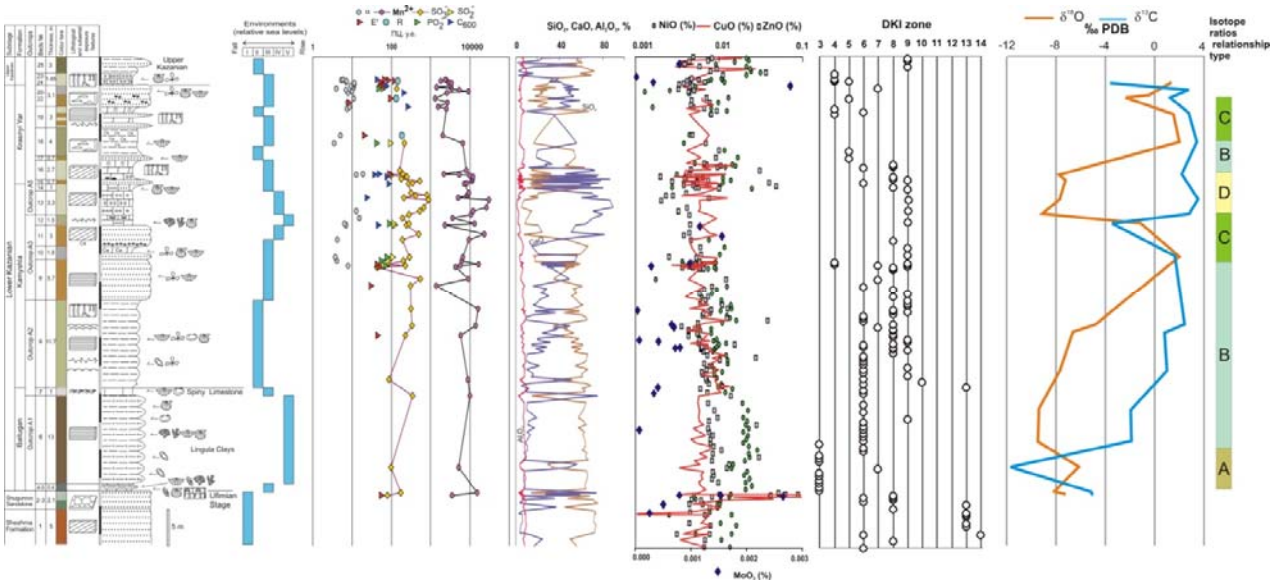

Figure-4. Summary section of the Lower Kazanian rocks (see legends on Figure-2) and geochemical variations. Depositional environments are explained in Table-1. Types of isotopic indicators correlation: A- decrease of $\delta^{13}C$ and increase of $\delta^{18}O$; B- increase of $\delta^{13}C$ and increase of $\delta^{18}O$; C- decrease of $\delta^{13}C$ and decrease of $\delta^{18}O$; D- increase of $\delta^{13}C$ and decrease of $\delta^{18}O$.$\delta^{18}O$, ‰ PDBwas calculated from $\delta^{18}O$, ‰SMOW.

On Figure-5 the distribution of the data in the coordinate field of isotope parameters of carbon and oxygen was shown. The position of data corresponds to set received in [9].

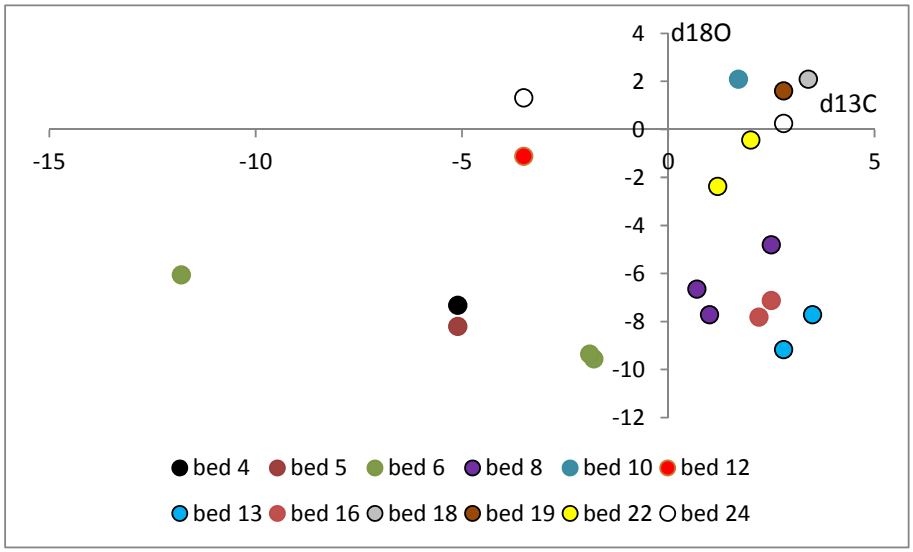

Figure-5. Isotope figures in two-dimensional coordinates (beds 4-22 - the Lower Kazanian substage;bed 24 - the Upper Kazaniansubstage).$\delta^{18}O$, ‰ PDB was calculated from $\delta^{18}O$, ‰ SMOW.

4. CONCLUSIONS

Variations of XRF, ESR and isotope data on reference surface section in South-Eastern Tatarstan reflect the changes in environmental history during the Early Kazanian at the east of the Russian platform and can be used as tool to develop the stratigraphic frame of the Biarmian Series.

ACKNOWLEDGEMENTS

The financial support of the RFBR scientific research project under 15-55-10007 project number and Russian Government Program of Competitive Growth of Kazan Federal University is gratefully acknowledged.

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