URZHUMIAN STAGE IN GEOCHEMICAL VARIATIONS

Nurgalieva N. G., Khaziev R. R., Gareev B. I. and Batalin G. A.
The Kazan Federal University, Insitute of Geology and Oil and Gas Technologies, Russia
E-Mail: nurlit@yandex.ru

ABSTRACT

Geological site Cheremushka is known as key stratigraphic record of Urzhumian stage of Middle Permian (Biarmian) series. It is situated on the Volga River's right bank, near Kazan city (Russia). In present paper lithology and geochemistry of this section is analyzed by EDXRF and discussed to reveal regional facial and cyclic features of the succession formed in altered sedimentary environments. Bulk geochemistry of sediments can be used to characterize the distribution of allogenic and authigenic components. It can also be used to compare these distributions with the general evolutionary stages of Volga River's region. The sedimentary sequence at site Cheremushka is divided into nine geochemical stages and sedimentary cycles using bulk geochemistry profiles, where silica change is considered as basic. The stage (cycles) boundaries correlate with the significant lithologic boundaries. Paleoenvironmental evolution is interpreted as alteration of lagoon and terrigenous flux influenced environments in arid climate during Sulitzkian time and in humid climate during Isheevskian time.

Keywords: urzhumian stage, X-ray fluorescence, bulk geochemistry, paleoenvironments.

1. INTRODUCTION

The East European Platform and Urals are stratotype regions of the Permian system, the only one of the twelve Phanerozoic geologic systems established in Russia by British scientist R.I. Murchison (1841).

The Permian East European basin is quite a large sedimentary basin, which was active from Carboniferous to Middle Triassic. From Kungurian times up to Middle Triassic, continuous accumulation of continental deposits took place here. Its paleogeographic position is also unique. On the one hand, it was located in a zone of temperately humid and temperately dry climate, which contributed to the prosperity of the biota and the formation of the rich fossil localities of continental organisms. On the other hand, the basin was located at the intersection of major global migration routes - from Gondwana to Laurasia and from Asia to Western Europe and North America.

Since 2001, a threefold division of the Permian with allocation of Middle Permian, Guadalupian, series of sections in the Guadalupe National Park in Texas, USA, and the Upper Permian, Lopingian, series of China sections has been introduced. Stratotypes of global significance are recorded in Russia only in the South Urals, and involve the determination of the boundaries of the Carboniferous and Permian, and stratigraphy of the Lower Permian series. However, it should be noted that the previously in Russia allocated Permian units continue to be used not only in a regional sense, but also, for example, for sections comprising marine and transitional facies in the Tethyan region.

Volga river's area near Kazan city is one of the few stratotype regions in the world in which knowledge of the Permian strata is unique and provided by vast data and ideal material, methodic and methodological approaches.

Not all aspects of the Permian sedimentary environmetns, facial composition and stratigraphy have been reached. For detailed interregional correlations of Permian sections biostratigraphic data are completely insufficient and the uses of additional physical and chemical correlation criteria are necessary.

Urzhumian Stage is upper part of Middle Permian (Biarmian) Series in reginal stratigraphic scheme. The rocks of Urzhumian age are observed at outcrops at Vyatka, Volga and Kama rivers. They contain record of a lot of geological processes related to paleoenvironmental changes in Middle Permian. These processes are mainly identified on sediments composition and fossil data.

In present paper new data on geochemistry by XRF along key sedimentary section Cheremushka have been regarded and discussed.

2. URZHUMIAN CHARACTERISTICS AT SITE CHEREMUSHKA

Urzhumian Stage was included into Middle Permian (Biarmian) series in 2005. It was stratigraphically distinguished by presence of non-marine bivalves [1]. Urzhumian stage at site Cheremushka begins from unconformity between Kazanian and Urzhumian Stages. It comprises lower (Sulitzkian) and upper (Isheevskian) suites (Figure-1).

Lithology and fauna characteristics of these suites were given in [1, 2]. The boundary between suites is the bottom of green clays layer with the first occurrence of non-marine bivalves [1]. This early Urzhumian association is represented by species *Palaeomutela olgae* Gus., *Prilukiella* sp., *Anadontella volgensis* (Gus.) belonging to a set of guide fossils.

Sulitzkian suite is composed of seven terrigenous and carbonate layers (layers 1-7 (Figure-1)) with rare fossils (fish flakes):

1. Sandstone (quartz arenite): brown; fine grained; subangular; locally clayey-silty. Thickness is 3.15 m.

VOL. 9, NO. 5, MAY 2014 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

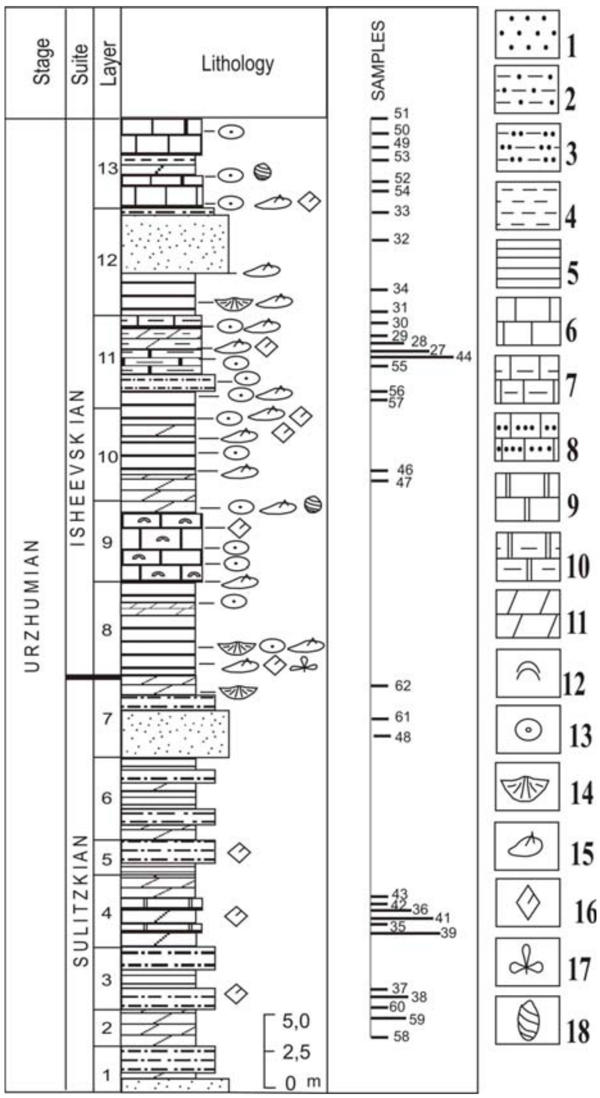

Figure-1. Lithological units of Urzhumian section.

Legends: 1- sandstones, **2-** siltstones, **3-** siltstones and sandstones, **4-** siltstones and claystones, **5-** claystones, **6-** limestones, **7-** clayey limestones, **8-** sandy limestones, **9-** dolomites, **10-** clayey dolomites, **11-** marls, **12-** stromatolites; **13-** fresh water ostracods, **14-** conchostracans, **15-** non-marine bivalves, **16-** fish flakes, **17-** plant remains, **18-** algae.

2. Marl: greenish and pinkish-gray; 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-gray; fine-grained and marl: gray; contained rare fish flakes. Thickness is 4.6 m.
4. Dolomite and marl: gray; 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-gray and brown; fine-grained; contained shells of conchostracans and fish flakes. Thickness - 2.55 m.
6. Alternation of marls: gray, 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): gray 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): gray; locally included claystone: red. Thickness is 5.55 m.

Isheevskian suite comprises of six terrigenous and carbonate layers (layers 8-13 (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-gray. 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: gray; cryptogenic; alternated with up marl dolomitic. Upper part contains limestones: gray; 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: gray; 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): gray and greenish-gray; 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: gray; 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.

VOL. 9, NO. 5, MAY 2014 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

Fourteen and twenty samples were collected from Sulitzkaya and Isheevskaya suites respectively (Figure-1) to study geochemical heterogeneity by XRF method.

3. XRF METHOD AND RESULTS

X-ray fluorescence (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 [3] 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.

Sixteen components (CaO, MgO, Al_2O_3, SiO_2, TiO_2, Fe_2O_3, K_2O, MnO, P_2O_5, S, Na_2O, Cl, Cr_2O_3, Sb_2O_3, Sn, Sm_2O_5, %) were determined by X-ray fluorescence (Figure-2). To process data it was used procedure from [4].

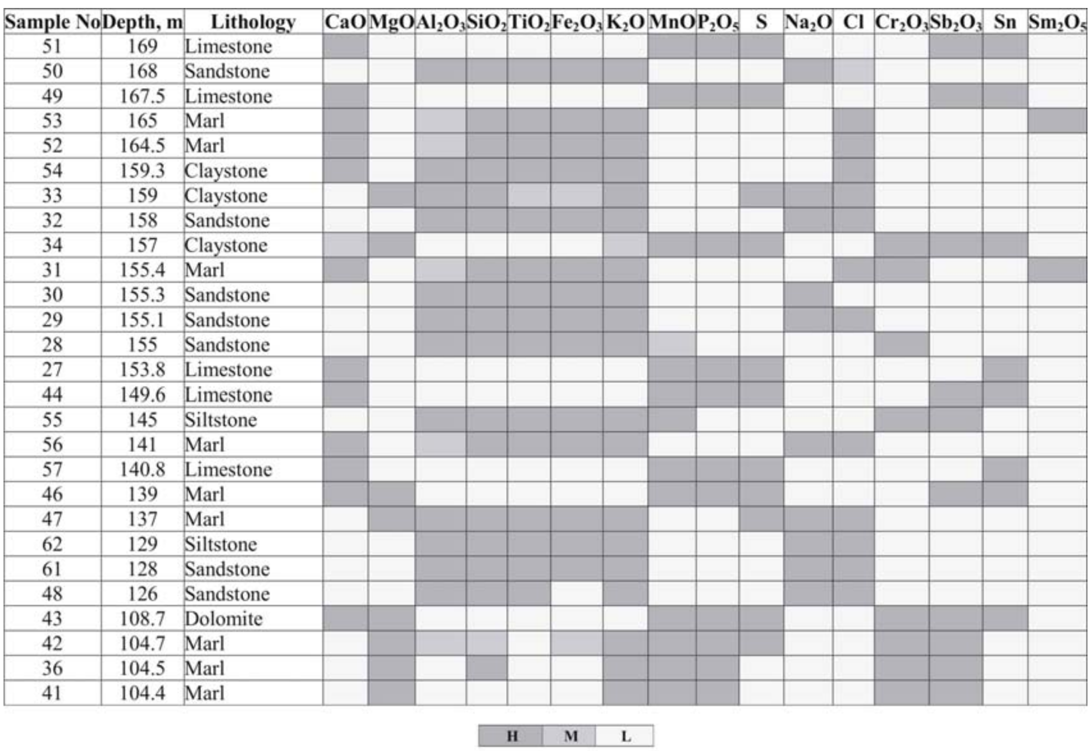

Figure-2. Geochemical image of Urzhumian section by collected samples XRF data.
H, M, L - values of content >, ≈, < mean value of data set, respectively.

Contents of representative elements are plotted as a function of silica contents for all samples in Figure-3. Titanium, aluminum, potassium, ferric iron, sodium show an increasing trend as silica increases. Calcium, magnesium, manganese, phosphorus and sulphur show a decreasing trend as silica increases.

VOL. 9, NO. 5, MAY 2014 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

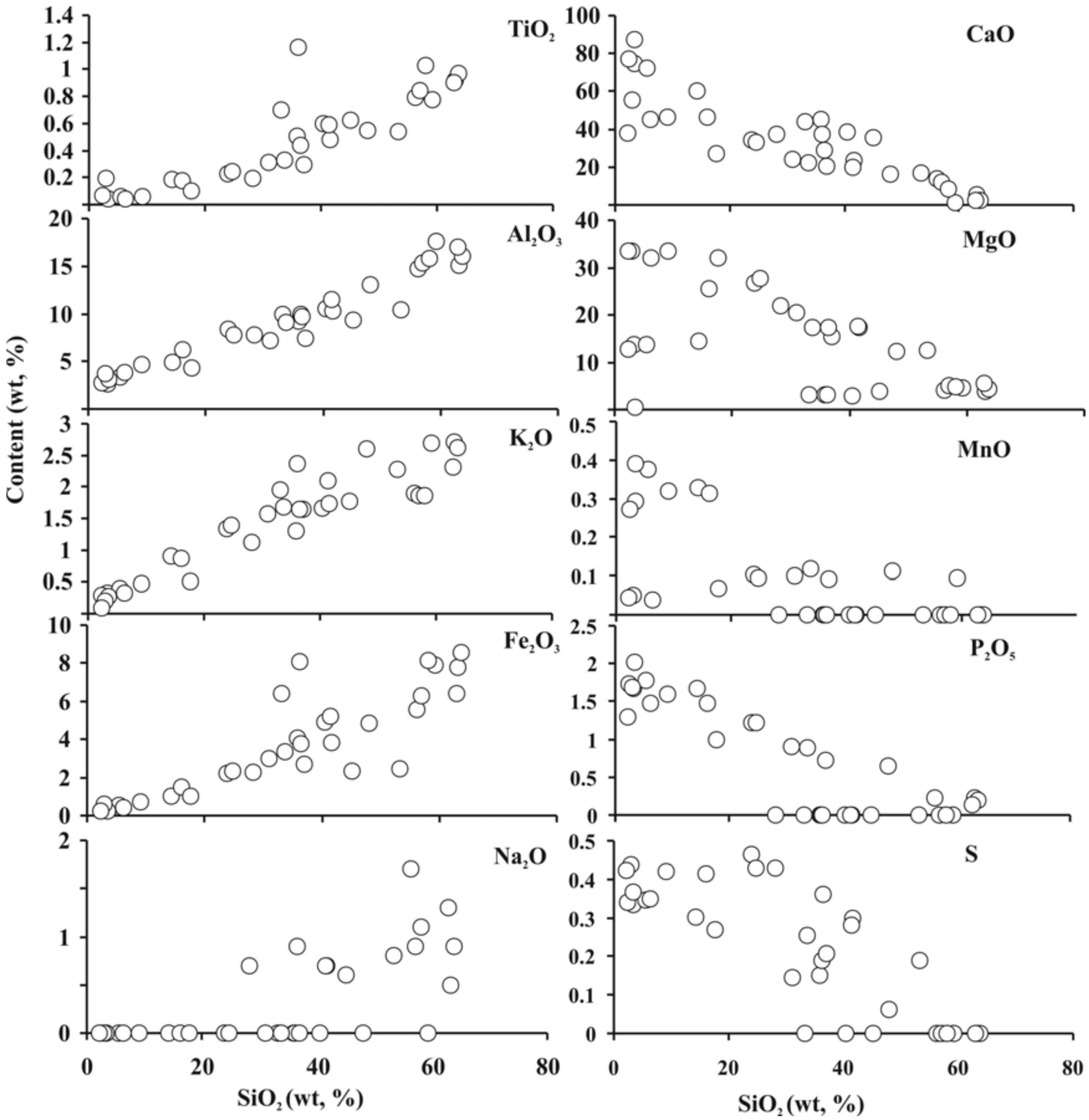

Figure-3. Variations in representative elements content (wt %) with increasing SiO_2 (wt %).

Depth profiles of the representative elements are shown in Figure-4.

Titanium, aluminum, potassium, ferric iron, sodium which show a simple increasing trend with increasing silica, basically show this direct pattern through the section (Figure-4). Profiles of elements such as calcium, magnesium, manganese, and phosphorus show reverse pattern with increasing silica along section (Figure-4). All trends are dependent on the trend of silica content. Therefore basic element for geochemical classification of Urzhumian section is just silica variation.

Nine geochemical stages and sedimentary cycles are distinguished from this variation: four in Sulitzkian suite and five in Isheevskian suite (Figure-5). Trace elements (Cr, Sb, Sn, Sm) variations are also suitable with these stages (Figure-6).

VOL. 9, NO. 5, MAY 2014 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

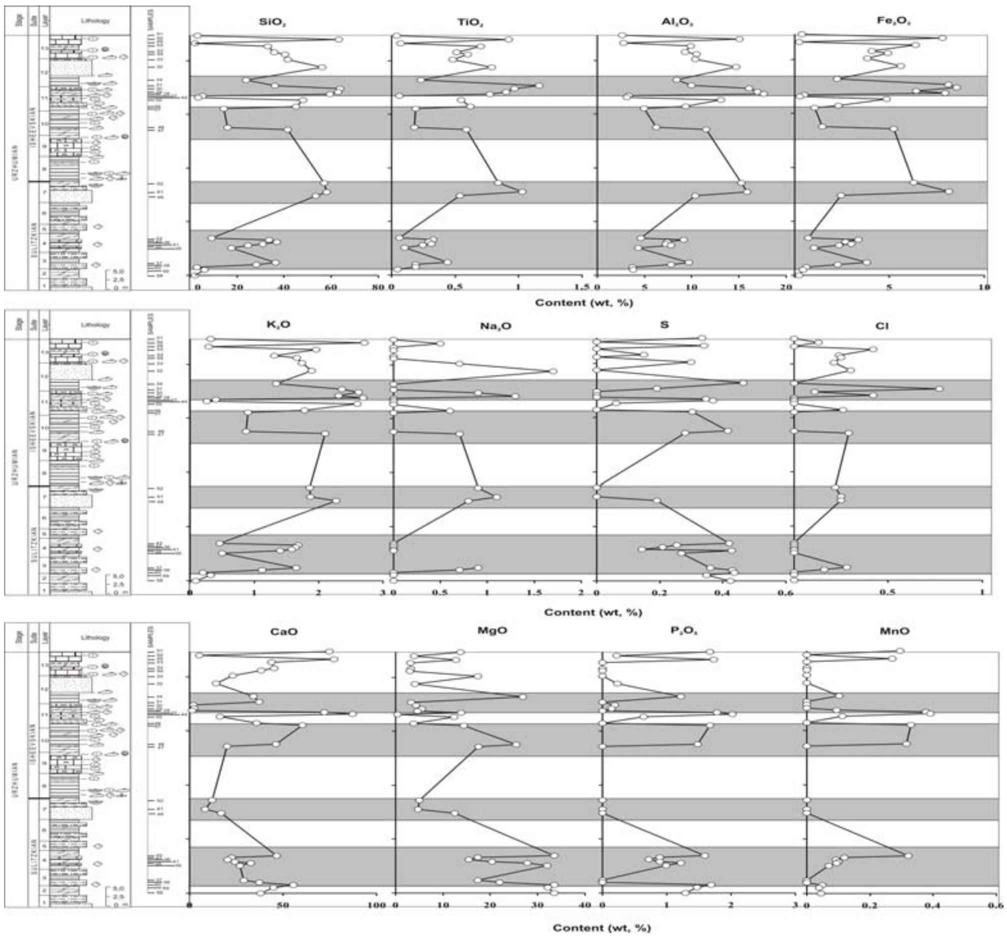

Figure-4. Variations in SiO_2, TiO_2, Al_2O_3, Fe_2O_3, K_2O, Na_2O, S, Cl, CaO, MgO, P_2O_5, MnO content (wt %) with depth, showing geochemical units.

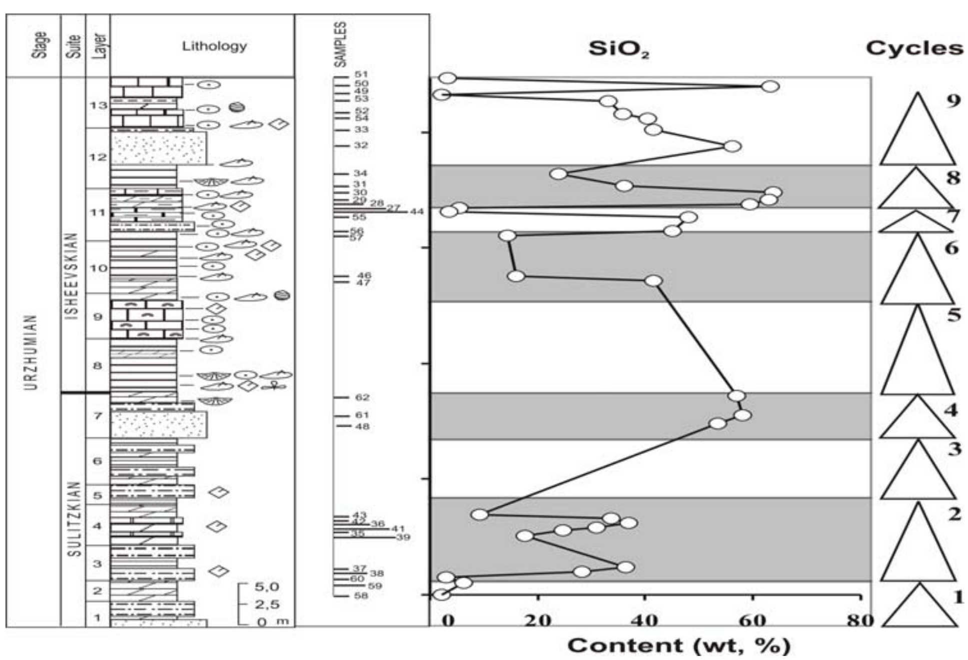

Figure-5. Silica as basic element to distinguish geochemical stages and sedimentary cycles.

VOL. 9, NO. 5, MAY 2014 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

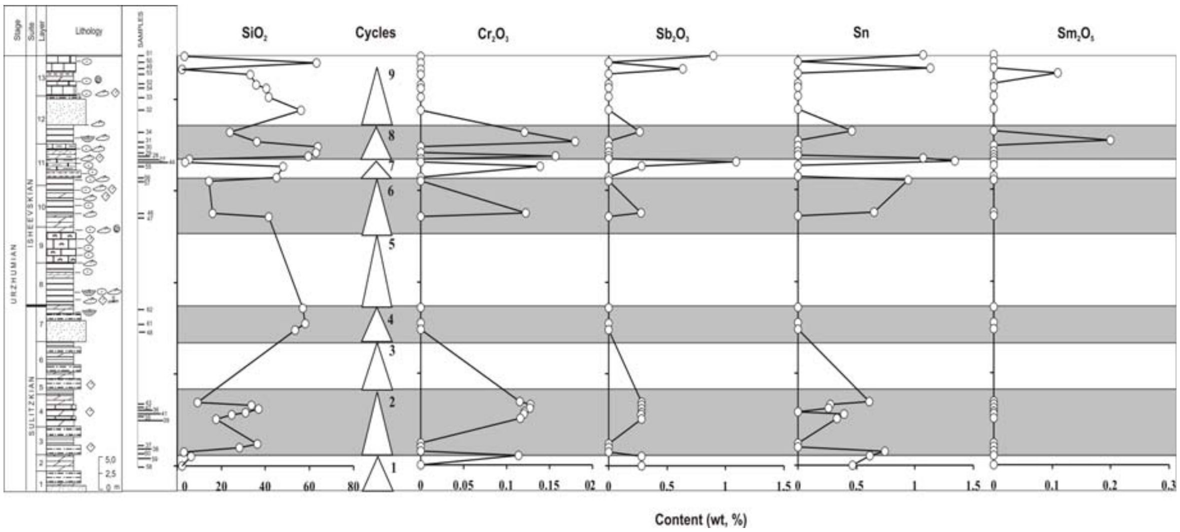

Figure-6. Trace elements in the geochemical stages and the sedimentary cycles.

Generally the lithological and the geochemical boundaries coincide. The cycle 1 includes the layers 1 and 2. The cycle 2 is a sum of the layers 3 and 4. The cycle 3 consists of the layers 5 and 6. The cycle 4 coincides with the layer 7. The cycle 5 correlates with a sum of the layers 8 and 9. The cycle 6 comprises of the layer 10 and a lower part of the layer 11. The short cycle 7 contains a middle part of the layer 11. The cycle 8 includes an upper part of the layer 11 and a lower part of the layer 12. The cycle 9 consists of an upper part of the layer 12 and almost the whole layer 13 (Figures 4, 5).

To recognize geochemical types of rocks we also used EPR data (Figure-7) from [3] and indexes by [5] (Figure-7): index CaO/(MgO+FeO+MnO) to distinguish geochemical types of carbonate rocks; HI (hydrolysis index) = (TiO2+Al_2O3+ +Fe2O3+FeO+MnO)/SiO2 to estimate role of components of weathering in rock composition; and TI (titanium index)= TiO_2/Al_2O_3 as indicator of rocks recycling.

4. INTERPRETATION OF DATA

Lithological variation and distribution of the geochemical parameters point on an expressive stratification of Urzhumian stage, where silica component is basic for geochemical stages-sedimentary cycles distinguishing (Figures 3-5, 7). It is an important component of detrital material of sedimentary rocks. Of the silicate minerals, feldspar and clay are the most abundant in detrital sedimentary rocks. In common, in sedimentary rock types, Si is predominantly found as detrital material produced during weathering [6]. Common source minerals include quartz and feldspar. Other forms of Si in sedimentary rocks include amorphous low temperature silicates, such as opal and chalcedony, formed during the process of diagenesis. They were not observed in Urzhumian rocks. Good direct correlation of silica with titanium, aluminium, ferric iron, potassium, sodium points on detrital provenance of these components accompanying silica.

The concentration of TiO_2 is determined by the abundance of detrital oxides and silicates, such as chlorite and clay minerals [6].

The content of Al_2O_3 increases from carbonates to sandstones and claystones. Claystones contain concentrations of Al_2O_3, due to the presence of clay minerals such as kaolinite. Although most naturally-occurring Al resides in feldspar minerals and their weathering and alteration products, Al tends to correlate with elements such as Fe and Cr in weathered material, and can be used, therefore, as an indicator for the presence of mafic rocks [6].

The abundance of Fe in sedimentary rocks is determined by various factors, including provenance, pH-Eh conditions, the extent of diagenetic alteration and grain size. In most instances, secondary hydrous oxides are the dominant Fe phases, although primary oxides may account for some of the iron. The tendency for hydrous Fe phases to form surface oxide coatings can be reflected in a direct relationship between total Fe content and the specific surface areas of sedimentary particles [6]. Hence, clay and greywacke are generally enriched relative to quartz-feldspathic sandstone and carbonate rocks.

The potassium content in claystones is primary a function of the clay mineral content, commonly illite. Impure carbonates tend to have K because of the occurrence of detrital silicate material (clays) in the non-carbonate fraction. Sandstones contain K in K-feldspar, K-mica and glaukonite. Mobility of K is limited by next processes: it is incorporated into clay mineral lattice because of large size; it is absorbed more strongly than Na^+ on the surfaces of clay minerals and organic matter [6].

The major sources of sodium in almost all detrital sedimentary rock types are detrital feldspar and clay minerals.

Increasing of chlorine is mainly explained by appearing of chlorite in clay minerals composition especially in cycles 8 and 9 (Figure-4).

 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

Presence of Cr can be explained by association with detrital phases such as chromite, magnetite and ilmenite [6]. During weathering, the behaviour of Cr^{3+} resembles that of Fe^{3+} and Al^{3+}, leading to widespread accumulation in secondary oxides and clays. Mainly concentration of Cr decrease from claystones through sandstones to limestones (Figure-5).

Increasing of Sb correlates in some cycles (1, 6-9) with fine-grained sediments [6] and reflects tendency for the element to become sorbed to hydrous oxides and clay minerals (Figure-6).

Sn dissolved during the weathering of mica may precipitate with Al-rich hydrolysates [6]. It is characterized by reverse pattern of variation in comparing with silica (Figure-6).

Sm is light rare-earth element (LREE). The REEs are generally dispersed as minor, non-essential elements in rock-forming minerals. Sphene and plagioclase tend to accommodate more LREEs [5]. The total REE abundance in sedimentary rocks tends to be lower than in igneous rocks. In general, REE content decreases with clay mineral and rock fragment content and increasing quartz content. Typical ranges of ΣREE in shale, greywacke, sandstone and limestone are observed as decreasing [6].

Terrigenous components of both suites are close to each other and consist of Si-Al and Si-Fe types of rocks on values of HI. TI values increasing correspond to beginnings of sedimentary cycles (Figure-7). Mean values of TI are 0, 038 and 0,049 for Sulitzkaya and Isheevskaya suites respectively. Silica (and direct connected accompaning elements) content in Isheevskaya suite is higher than the same in Sulitzkaya suite. Hence terrigenous flux during cycles 5-9 was more intensive than during cycles 1-4. Radiation centers $E^{'}$ in quartz (EPR data) coincide with lower part of cycles 4, 7, 8, 9 (Figure-7). The presence of pointed paramagnetic centers, probably, evidence about specific composition of source rocks subjected to thermal activation [7].

Calcium, magnesium, manganese, phosphorus and sulphur show reverse pattern with increasing silica along section (Figure-4). Hence limestone and dolomite are carbonate sediments that are an important sink for these elements. Ca is indicative of calcareous rocks, especially in association with Mg, Mn, P and S.

Carbonate component of Sulitzkian suite is characterized predominantly by Ca (Fe) Mg and Mg (Fe) Ca geochemical types. Isheevskian suite is composed mainly of Ca types of carbonate rocks (Figure-7). On EPR data Mn^{2+} content decreases with SiO_2 increasing. Increasing of ratio α (ratio of Mn^{2+} in dolomite in Mg and Ca positions respectively) points on primary provenance of dolomite crystals in sediments (Figure-7).

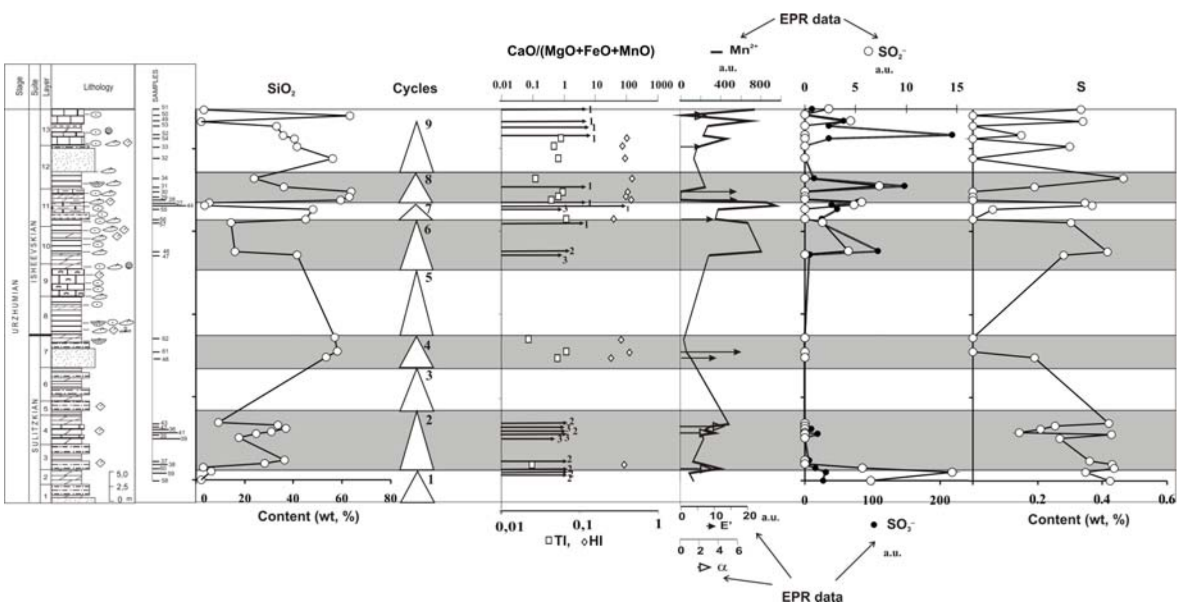

Figure-7. Geochemical stages and sedimentary cycles in geochemical indexes on XRF and EPR data. On index CaO/(MgO+FeO+MnO) carbonate rocks types are distinguished: 1 - Ca class; 2 -Mg (Fe) Ca class; 3 - Ca (Fe) Mg class.

Sulphur variations correlate with sulphate-radicals concentrations in carbonate material on EPR data (Figure-7). They can be interpreted as indicators of hydrochemical environment changing that were more significant in cycles 2 and 8.

Two lower cycles of Sulitzkian suite can be interpreted as saline lagoon environmental ones formed in arid climate (absence of fossils; high values of α; Ca (Fe) Mg and Mg (Fe) Ca types of carbonate rocks; halite crystals in layer 4). Two upper cycles of suite can be described as terrigenous flux (river channels) influenced cycles (Si-Al and Si-Fe types of terrigenous rocks).

Three lower cycles of Isheevskian suite we interpret as fresh-water lagoon cycles (fresh water fauna, Ca types of carbonate rocks, Si-Al and Si-Fe types of terrigenous rocks, clay minerals composition) and cycles 8 and 9 can be interpreted as terrigenous flux (river channels) influenced cycle (sandstone: polymictic cross bedded) with local salinity increasing (sulphates content deviations).

5. CONCLUSIONS

The sedimentary record of Urzhumian at site Cheremushka is a fascinating succession that furthers our understanding of how geochemical and sedimentary data respond to paleoenvironmental change. This paper shows clearly how the bulk geochemistry of sediments can be used to characterize the distribution of allogenic and authigenic components. It can also be used to compare these distributions with the general evolutionary stages of Volga River’s region.

The sedimentary sequence at site Cheremushka is divided into nine geochemical stages and sedimentary cycles using bulk geochemistry profiles, where silica change is considered as basic. The stage (cycles) boundaries correlate with the significant lithologic boundaries. Paleoenvironmental evolution is interpreted as alteration of lagoon and terrigenous flux influenced environments in arid climate within Sulitzkian time and in humid climate within Isheevskian time.

This work was funded by RFBR [13-05-00642] and the subsidy of the Russian Government to support the Program of competitive growth of Kazan Federal University among world class academic centers and universities.

REFERENCES

[1] Геология Приказанского района. Путеводитель по полигонам учебных геологических практик - Под редакцией А.И.Шевелева. - Казань: ЗАО «Новое знание», 2007. - 208 с. (Geology of Prikazanskian area. Guide to outcrop geological experience. 2007. Ed. A.I. Shevelev. Kazan: ZAO Novoye znaniye. p. 208. In Russian).

[2] Нургалиева Н.Г., Хасанова Н.М., Габдрахманов Р.Р. Условия образования уржумских отложений по данным ЭПР // Ученые записки Казан. Ун-та. Сер. Естеств.науки.- 2010. - Т.152, кн.1.-С.226-234. (Nurgalieva N. G., Khasanova N.M., Gabdrakhmanov R.R. 2010. Formation of Urzhumian sediments by EPR data. J. Uchenye Zapiski Kazanskogo Universiteta. Series Natural sciences. 152(1): 226-234. in Russian).

[3] S2 RANGER. Spectromentry solutions. http://www.bruker.com/fileadmin/user_upload/8-PDF-Docs/X-rayDiffraction_ElementalAnalysis/XRF/Brochures/S2_RANGER_Brochure_DOC-B80-EXS006_en.pdf.

[4] Saito S. 1998. Major and trace element geochemistry of sediments from east Greenland continental rise: an implication for sediment provenance and source area weathering. Saunders, A.D., Larsen, H.C., and Wise, S.W., Jr. (Eds.). Proc. ODP, Sci.Results, 152: College Station, TX (Ocean Drilling Program). pp. 19-28.

[5] Юдович Я.Э., Кетрис М.П. Основы литохимии. - СПб: Наука, 2000. - 479 с. (Yudovich Ya. E., Ketris M.P. 2000. Lithochemistry basis. S.-P.: Nauka. p. 479. In Russian).

[6] Geochemical Atlas of Europe. Ed. R. Salminen. FOREGS. A contribution to IUGS/IAGC Global Geochemical Baselines. weppi.gtk.fi/publ/foregsatlas/index.php.

[7] Лютоев В.П., Силаев В.И. Типоморфизм парамагнитных центров в структуре кварца из уральского редкометалльного месторождения - Mineral. Journ. (Ukraine). - 2008. - 30, No 2. - P.64-74 (Lutoev V.P., Silaev V.I. 2008. Typomorphism of paramagnetic centres in quartz structure from Uralian REE deposit. Mineral. Journ. (Ukraine). 30(2): 64-74 In Russian) - archive.nbuv.gov.ua/portal/natural/mineral/2008_2/5.pdf.