TRACE ELEMENT GEOCHEMISTRY OF THE PLIOCENE SEDIMENTS, THE SOUTH CASPIAN BASIN

Based on study of the trace element composition of the Pliocene Productive Series sediments exposed in the Kirmaki and Yasamal Valleys located in the Absheron Peninsula, a number of paleoenvironmental indicators were identified. It was shown based on study of the strontium to barium ratio that the highest salinity was in the Fasila Suite sedimentary basin. The Balakhani and Sabunchy Suites' sediments were accumulated in a brackish-water environment. A general trend of the salinity decrease from the PreKirmaki Suite to the PostKirmaki Clay Suite is recorded in the lower portion of the Productive Series.

Also, it was recorded that in the case of migration of element in the form of solution, its maximum occurs in the muddy sediments of the deep-water zone wheares under condition of transportation of an element by clastic particles, its maximum concentration is reported in sandy sediments of the shoreface zone.

Keywords: the South Caspian basin, Pliocene Productive Series, trace elements, salinity, order factor

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Geological background

Sedimentation in the South Caspian basin in the beginning of Pliocene occurred under conditions of small, closed basin, isolated from the Eastern Paratethys due to intensive orogenic movements, uplifts of the adjacent land, subsidence of central part of the South-Caspian depression and fall of the Caspian Sea level that reached according to some estimations 600 m (Reynolds et al., 1998).

The Pliocene South Caspian succession referred to as "the Productive Series" is a fluvial-deltaic and lacustrine depositional system. The early phase of deposition was mostly controlled by the incision of the Paleo-Volga, which delivered large volumes of terrigenous clastics into the basin.

The Productive Series (PS) succession is composed of the rhythmically alternating sandy-shaly sediments reaching the thickness of 7 km in the deeply subsided parts of the South-Caspian depression.

It consists of 9 Suites (Gala (KaS), Prekirmaki (PK), Kirmaki (KS), Post Kirmaki sand (NKP), Post Kirmaki clay (NKG), Fasila, Balakhani, Sabunchi, Surakhani), and occurs in a large area – Absheron peninsula, Absheron and Baku archipelagos, Jeyrankechmez depression, Alyat ridge, Pre-Caspian-Guba region.

The PaleoVolga sediments have been extensively studied during XIX, XX, XXI centuries. The most attention was paid to the lithology, environmental changes, oil-gas prospects. However, many questions remain unexplored. This paper is aimed at addressing the controlling factors on microelemental quantification, particularly, relationship between environmental and microelemental variations.

The research is focused on the microelemental response in the small order forestepping and backstepping PaleoVolga deltaic sequences formed as a result of changing balance between sediment supply and lake levels controlled by climatic changes.

The addressed questions have been studied on the large amount of the PaleoVolga sediment samples exposed in the Absheron peninsula: the lower portion of the PS succession – in the Kirmaki Valley, the upper portion – in the Yasamal Valley.

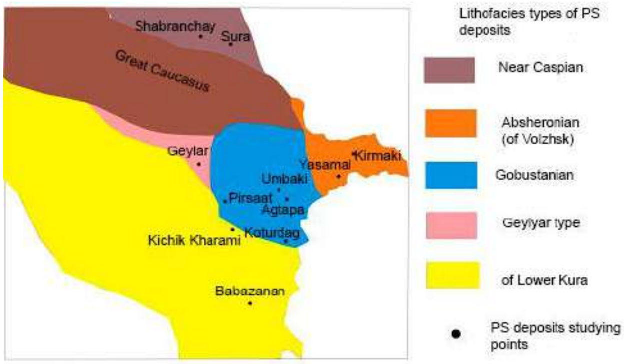

Figure 1. The map of the Productive Series sediments occurrence (from Aliyeva E., 2008)

Main results

Microelements in studied sediments were analyzed by X-ray method.

The results are presented in Tables 1, 2, 3 which are organized by different lithological varieties of sediments.

On the whole average contents of microelements, except Sr and Mn in shales and silts is higher than in sands, and variations of their quantities are more pronounced in sandstones. The similar distribution in sandstones and shales is recorded only for strontium.

The microelemental variations along the PS section demonstrate some patterns. We grouped these trace elements by similarities of their distribution.

Five groups are distinguished: 1) Ba, Ti, V (Figure 2; Figure 3); 2) Fe, Co, Ni, Cr, Cu, Zn (Figure 4; Figure 5), Pb (Figure 6); 4), Sr (Figure 7) and 5) Mn (Figure 8).

Elements of the first group (Ba, Ti, V) form a deep minimum in the NKP and Fasila Suites, and clearly expressed maximums in sediments of Kirmaki (KS), NKG and Sabunchi Suites.

Elements of the second group (Fe, Co, Ni, Cr, Cu, Zn) have one deep minimum in the NKP Suite sediments, one strong maximum in the NKG succession, and less expressed maximums in the Kirmaki and Sabunchi Suites (Figure 4; Figure 5), i.e. maximums are similar to those ones in group I (Figure 2; Figure 3).

The members of the third group consisting of just one trace element – lead, display an inverse behavior with respect to the first and second groups. The maximum of Pb amount is recorded in the NKP and Fasila Suites, minimum – in NKG and Balakhany Suites (Figure 6).

Elements of the forth group (Sr) is characterized by one minimum in NKG Suite sediments, and maximum in the PK and Surakhany Suites (Figure 7).

Maximum in Fasila and two minimums in PK and Surakhany Suites successions are recorded in the fifth group consisting of Mn (Figure 8).

The analyzed curves of the trace element content values variations in the Productive Series demonstrate that mudstones are depleted by a number of elements – Ba, Sr, Mn, Fe, Cr, Co, Ni, Pb, regarding to their clark values. Clark exceeding average cintent values have been recorded only for Ti (1.5 times higher), and V (2 times higher) in all suites shales and siltstones excepting PK Suite (Table 1, 2).

For the sandstones the amount values variations demonstrate inverse character. These sediments are enriched by Ba (the average amount 5–10 times exceeds the clark values), Sr (average content is 10 times higher than clark value), Mn (10–100 times higher), Fe (2–3 times exceeds), Co (5–10 times exceeds), Ni (5–10 times higher), Zn (2–5 time higher), Cu (5–10 times higher than clark value), Pb (2 times higher). The PS sandstones are depleted by Cr, Ti, V relative to clark values (Table 3).

Trace elements show divers behavior in the different stratigraphic unites of the Productive Series displaying various lithology.

The PK Suite is characterized by most heterogeneity that is characterized by growth of Co, Cu, Pb, Cr and Ni content values from sandstones to siltstones, and vice-versa distribution of Fe, Mn, Ba, Ti, Zn, Sr and V (Figure 9).

Table 1

Distribution of trace elements in the PS shales

Horizon	**Ba**	**Sr**	**Mn**	**Ti**	**Fe**	**V**	**Cr**	**Co**	**Ni**	**Zn**	**Cu**	**Pb**
PK												
KS	0.054	0.028	0.056	0.61	3.96	0.027	0.0033	0.0011	0.0029	0.0097	0.0076	0.0012
NKP	0.054	0.020	0.029	0.60	3.84	0.027	0.0042	0.0015	0.0041	0.0079	0.0043	0.0024
NKG	0.055	0.024	0.038	0.60	4.34	0.027	0.0011	0.0014	0.0037	0.0118	0.0038	0.0026
Break suite	0.051	0.033	0.015	0.61	4.19	0.026	0.0017	0.001	0.0058	0.015	0.008	0.0007
Balakhany	0.051	0.022	0.032	0.60	4.65	0.025	0.0064	0.0019	0.0058	0.0087	0.0044	0.0017
Sabuncni	0.053	0.025	0.065	0.61	4.08	0.026	0.0039	0.0013	0.0042	0.011	0.0041	0.002
Surakhany	0.053	0.032	0.065	0.60	3.98	0.025	0.0047	0.0012	0.0049	0.0091	0.0034	0.0016

Table 2

Distribution of trace elements in the PS silts

Horizon	**Ba**	**Sr**	**Mn**	**Ti**	**Fe**	**V**	**Cr**	**Co**	**Ni**	**Zn**	**Cu**	**Pb**
PK	0.020	0.030	0.010	0.22	1.01	0.014	0.0075	0.0008	0.0019	0.0025	0.0055	0.002
KS	0.052	0.023	0.054	0.61	3.11	0.027	0.0034	0.0018	0.0033	0.0073	0.0051	0.0016
NKP												
NKG	0.051	0.022	0.061	0.61	3.66	0.024	0.0044	0.0009	0.0009	0.015	0.007	0.0008
Breat suite												
Balakhany	0.054	0.019	0.031	0.60	4.71	0.026	0.006	0.0017	0.0054	0.01	0.0058	0.0018
Sabuncni	0.053	0.025	0.047	0.62	4.40	0.025	0.0023	0.0013	0.004	0.011	0.0038	0.001
Average by:												
Turekian and												
Wedepohl, 1961	**0.058**	**0.03**	**0.085**	**0.46**	**4.72**	**0.013**	**0.009**	**0.0019**	**0.0068**	**0.0095**	**0.0045**	**0.002**
Vinogradov, 1962	**0.08**	**0.045**	**0.067**	**0.45**	**3.33**	**0.013**	**0.01**	**0.002**	**0.0095**	**0.008**	**0.0057**	**0.002**

Table 3

Distribution of trace elements in the PS sands

Horizon	**Ba**	**Sr**	**Mn**	**Ti**	**Fe**	**V**	**Cr**	**Co**	**Ni**	**Zn**	**Cu**	**Pb**
PK	0.031	0.043	0.021	0.42	1.28	0.021	0.001	0.0007	0.0014	0.004	0.002	0.0011
KS	0.035	0.038	0.048	0.41	1.91	0.019	0.0034	0.0008	0.0019	0.0047	0.0028	0.0012
NKP	0.019	0.023	0.083	0.08	0.60	0.011	0.0007	0.0004	0.0005	0.0016	0.0015	0.0015
NKG	0.029	0.019	0.103	0.35	4.88	0.016	0.0016	0.0011	0.003	0.0085	0.0047	0.0008
Break suite	0.012	0.025	0.153	0.10	2.18	0.008	0.0028	0.0009	0.0020	0.0032	0.0027	0.0017
Balakhany	0.025	0.025	0.113	0.29	1.48	0.015	0.0027	0.0008	0.0018	0.0036	0.0018	0.0011
Sabuncni	0.032	0.035	0.071	0.40	2.05	0.029	0.0029	0.0008	0.0020	0.0049	0.0031	0.0015
Surakhany	0.023	0.054	0.037	0.27	1.42	0.014	0.0023	0.0006	0.0012	0.0042	0.0020	0.0014
Average by:												
Turekian and												
Wedepohl, 1961	**$n*10^{-3}$**	**0.003**	**$n*10^{-4}$**	**0.15**	**0.98**	**0.002**	**0.0035**	**$3*10^{-5}$**	**0.0002**	**0.0016**	**$n*10^{-4}$**	**0.0007**

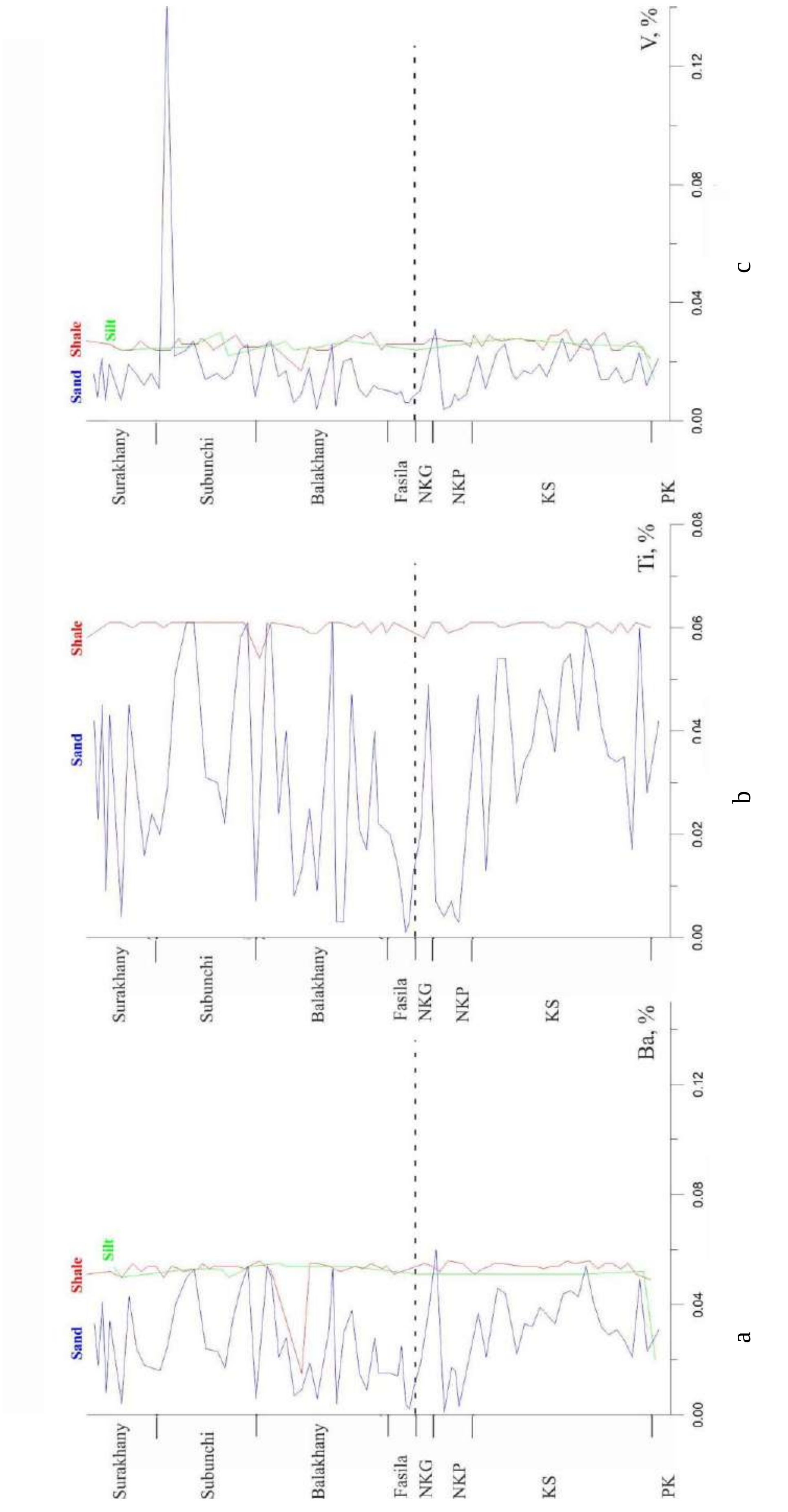

Figure 2. The plot displaying the Ba, Ti, V quantity variations in the ProductivepSeries section

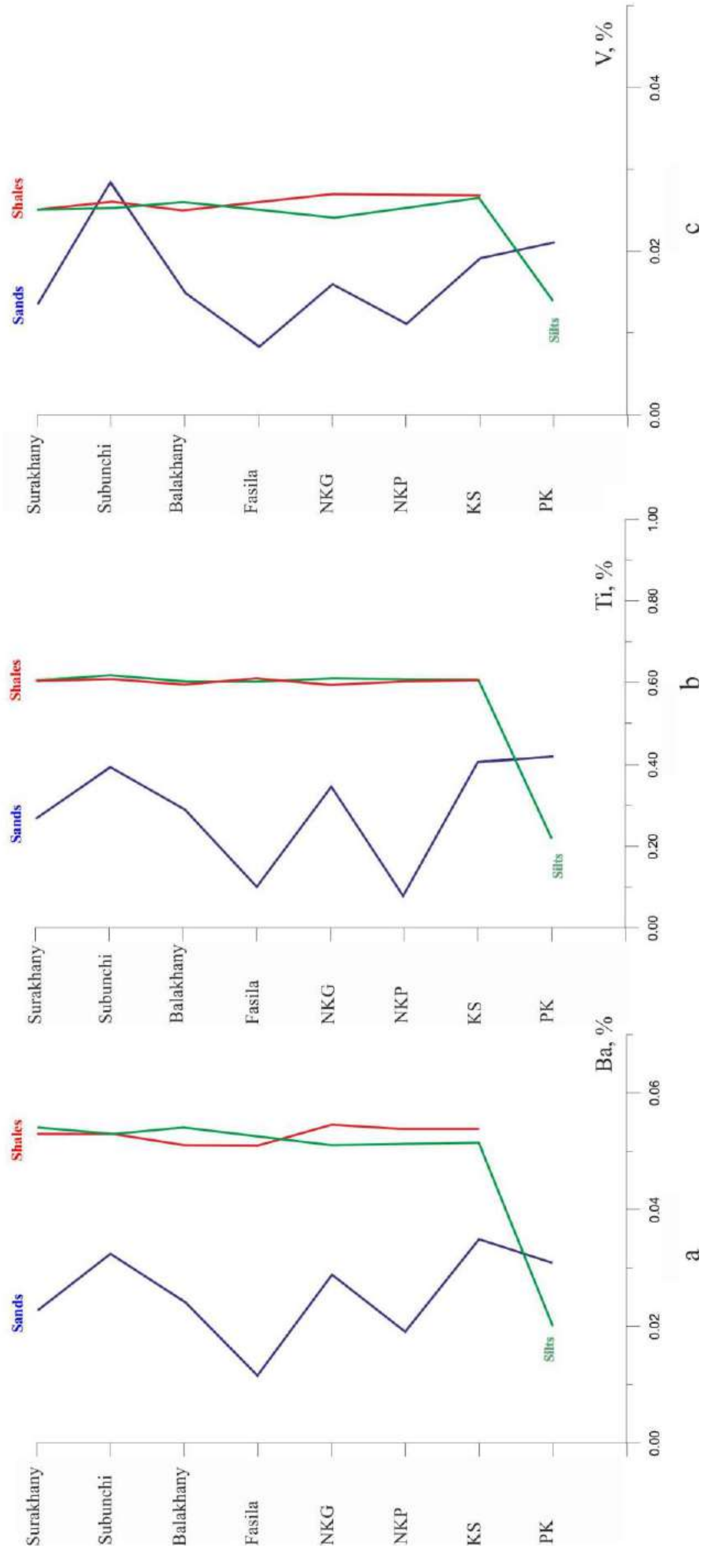

Figure 3. The plot displaying variations of the Ba, Ti, V average contents in the Productive Series section

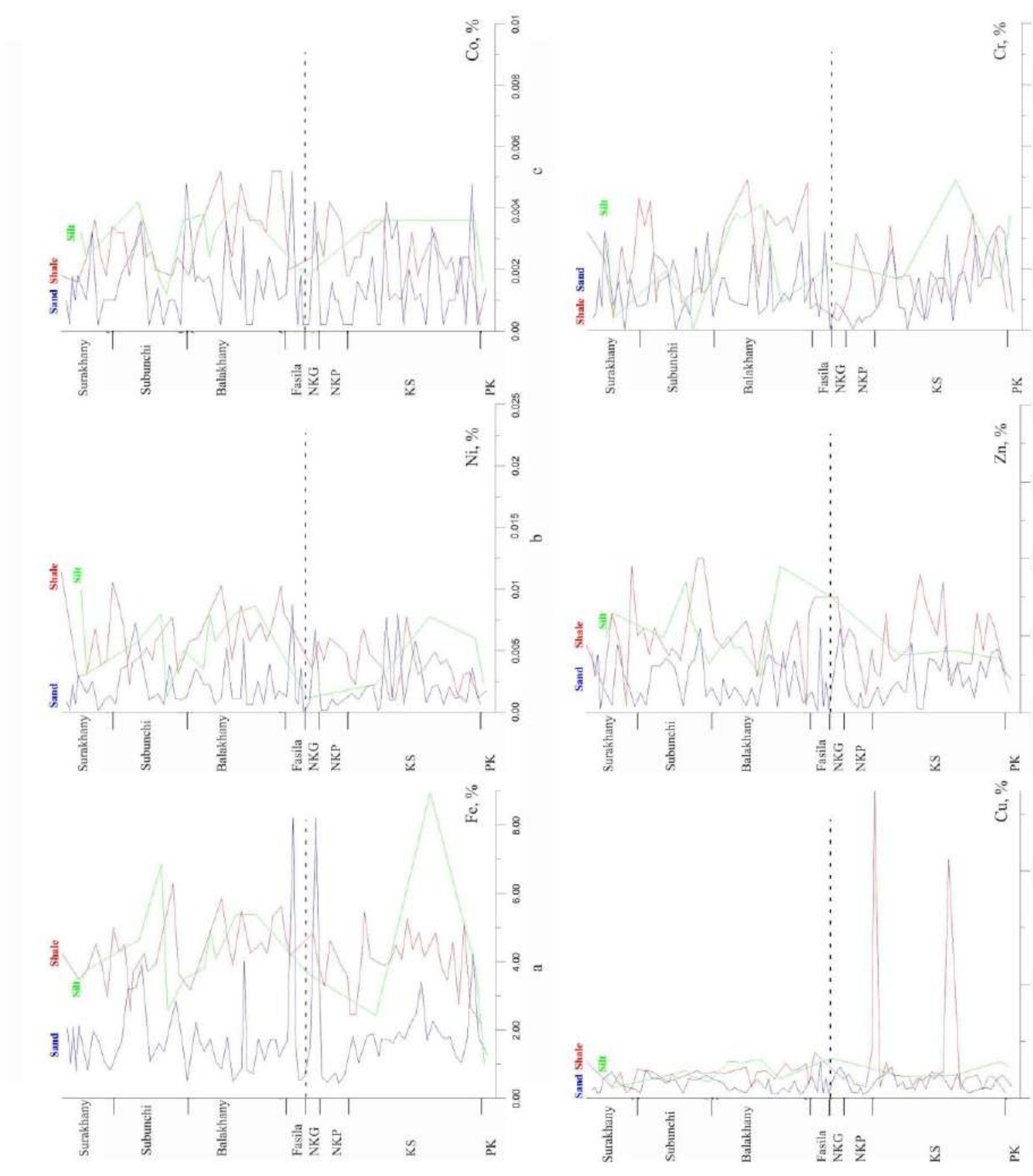

Figure 4. The plot displaying the Fe, Ni, Co, Cu, Zn, Cr quantities variations in the Productive Series section

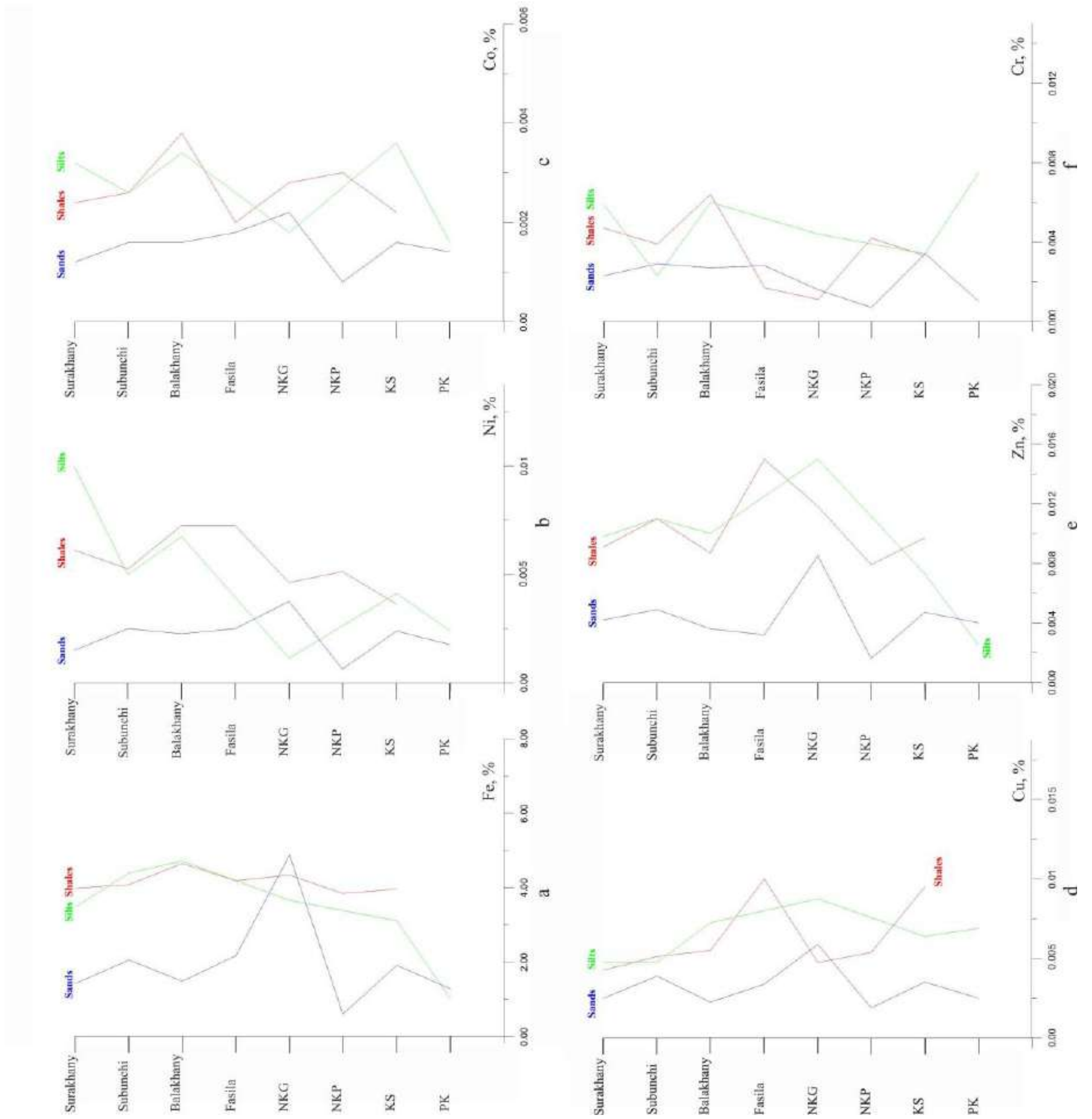

Figure 5. The plot displaying variations of the Fe, Ni, Co, Cu, Zn, Cr average contents in the Productive Series section

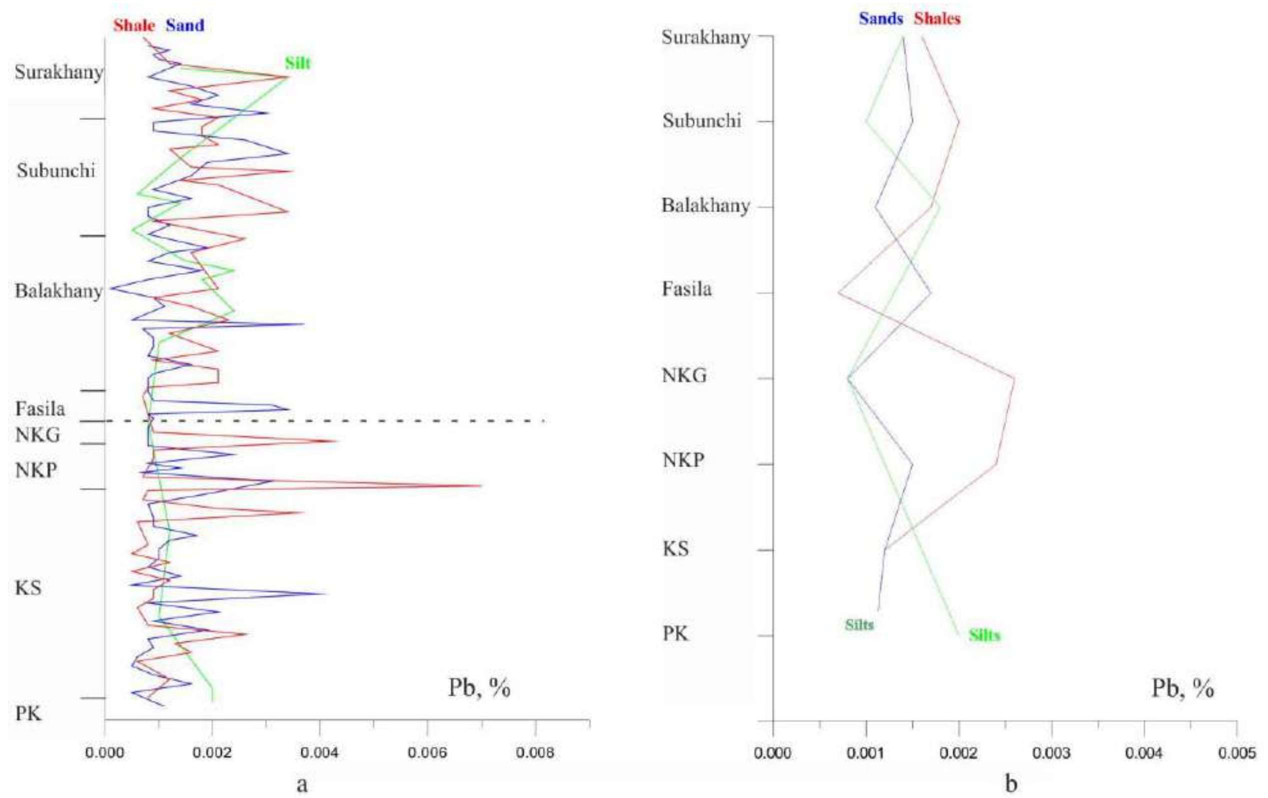

Figure 6. Lead content values variations along the Productive Series section.
a. lead amount in all analyzed samples of the various PS suites; **b.** lead average content in the various PS suites

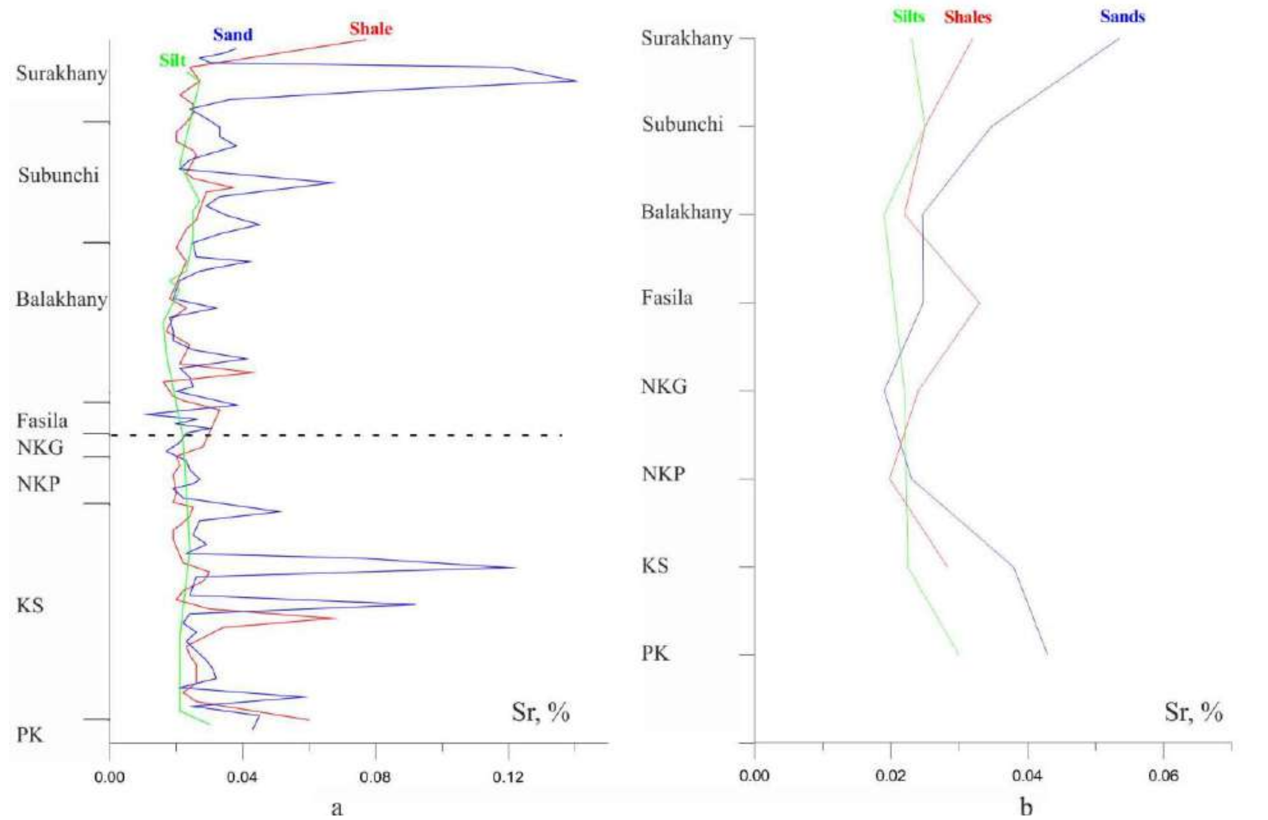

Figure 7. Strontium content values variations along the Productive Series section.
a. Sr amount in all analyzed samples of the various PS suites; **b.** Sr average content in the various PS suites

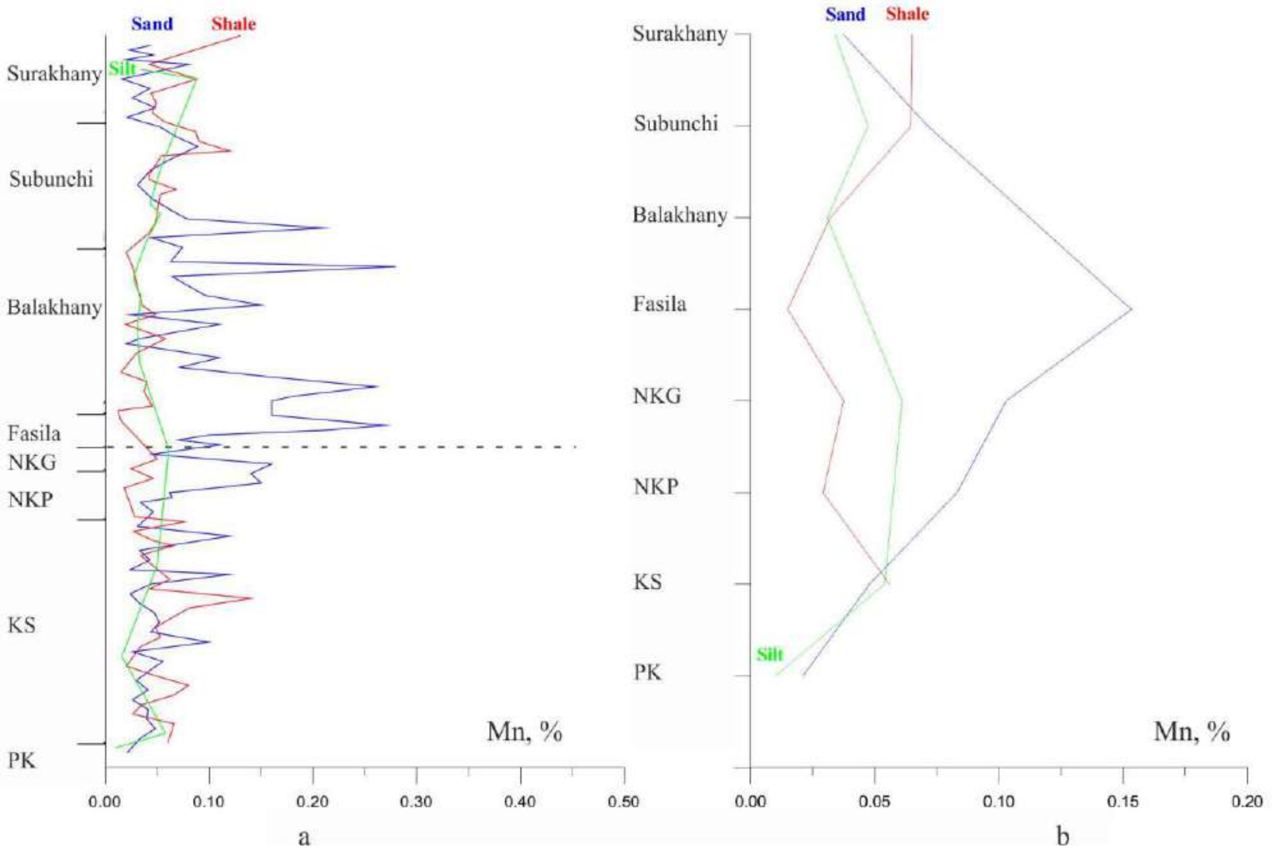

Figure 8. Manganese content values variations along the Productive Series section.
a. Mn amount in all analyzed samples of the various PS suites; **b.** Mn average content in the various PS suites

Distribution of elements in sediments of the Kirmaki Suite becomes more uniform (Figure 9). Only two elements Cr and Sr stand out. Clear trend of element content value growth from sandstones to siltstones and shales is observed for six elements (V, Fe, Ba, Mn, Cu and Zn). The rest four elements (Co, Ni, Ti, Pb) display their maximum in siltstones.

The NKP Suite sediments are characterized by a growth of amount of almost all elements from sandstones to shales excluding Sr and Mn that display the opposite trend (Figure 9).

In the NKG Suite sediments only 4 elements – Pb, Sr, V and Ba demonstrate a clear trend of content value increase from coarse sediments to fine (Figure 9). The rest elements do not have any regularity of their distribution.

The same trend is observed in the Fasila Suite sediments excepting quantities of Mn, Pb and Cr that vary in the opposite manner (Figure 10).

In the Balakhany Suite sediments the described above trend of the element content values increase from sandstone to siltstones and shales is observed in the Cr, Ni, Co variations. No trend is recorded in the Mn and Sr behavior. For 7 elements – Pb, V, Fe, Ba, Cu, Ti, Zn, the maximum values fall to siltstones (Figure 10).

In the Sabunchi Suite sediments only two elements – Cu and Ni, have the gradual amount growth from coarse to fine grained varieties (Figure 10). For the most trace elements no clear trend is observed.

The same is true for the Surakhany Suite (Figure 10).

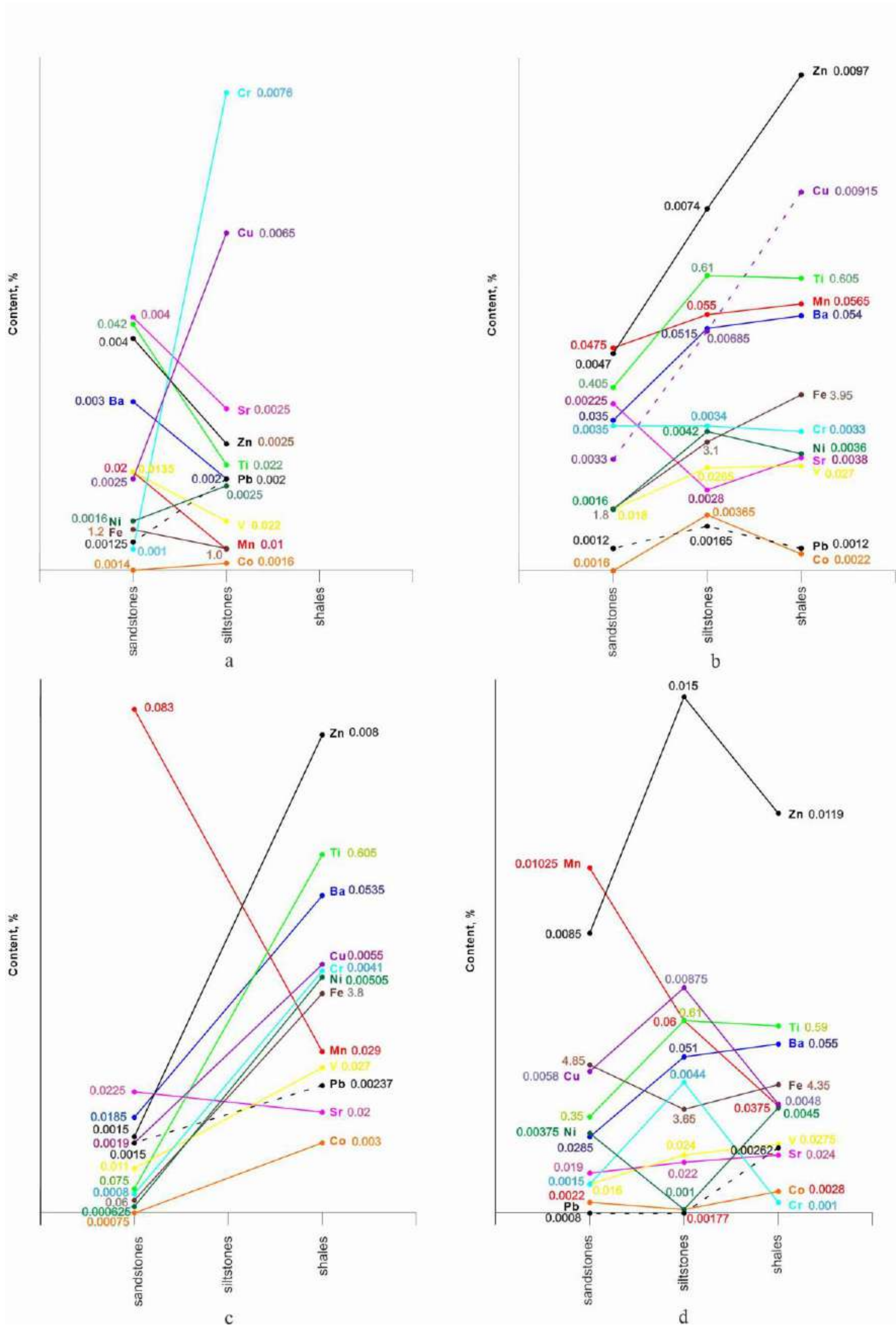

Figure 9. Trace elements content values variations between different lithological sediment varieties of the lower portion of the Productive Series: **a.** the PK Suite; **b.** the Kirmaki Suite; **c.** the NKP Suite; **d.** the NKG Suite

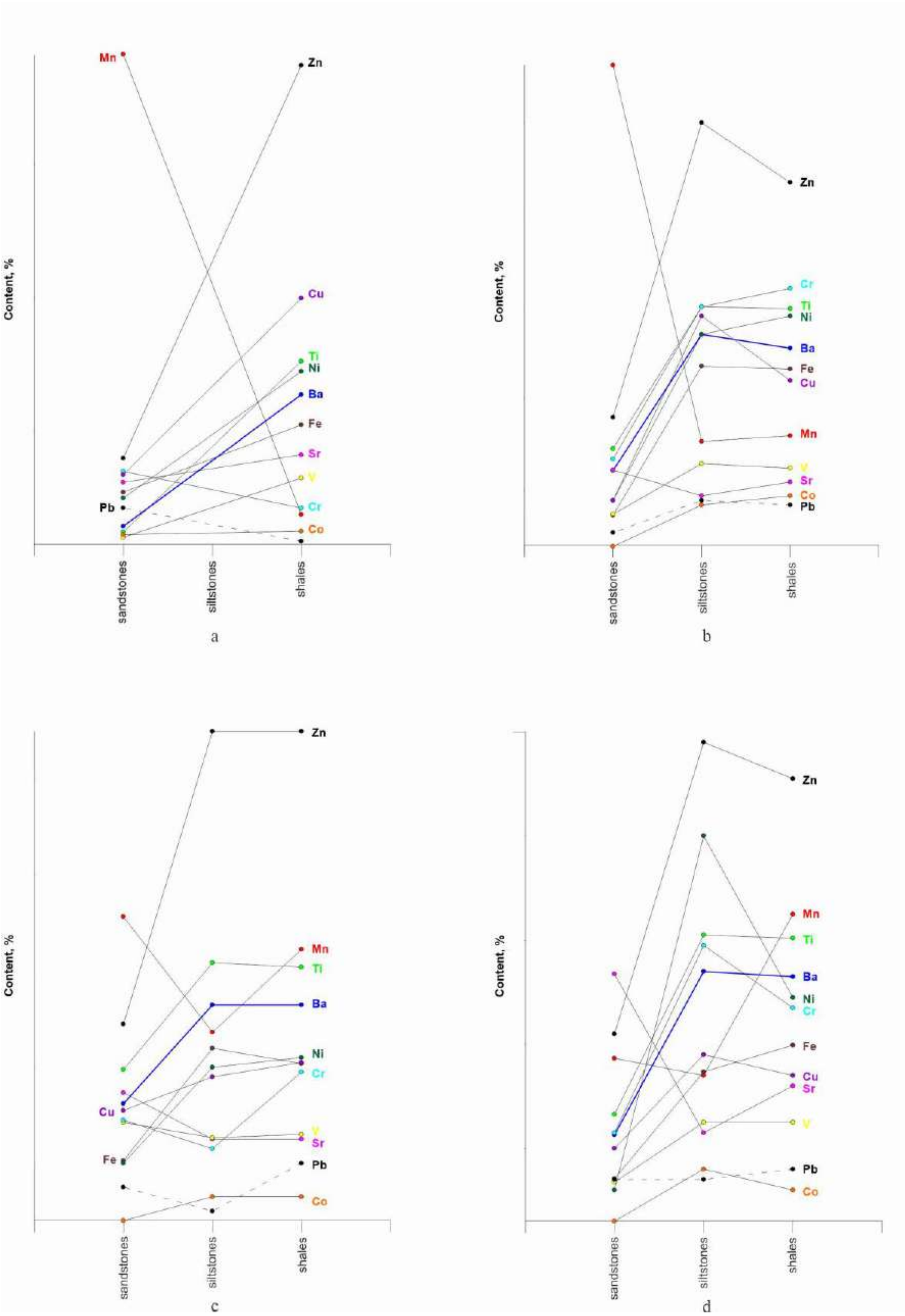

Figure 10. Trace elements content values variations between different lithological sediment varieties of the upper portion of the Productive Series: **a.** the Fasila Suite; **b.** the Balakhany Suite; **c.** the Sabunchi Suite; **d.** the Surakhany Suite

In the river water elements migrate with the terrigenous clasts, suspension or in the solution. The same element can migrate in the different ways that is determined by mineral composition of parent rocks. For instance, the common minerals of Fe are limonite, hematite, siderite, ilmenite, titanomagnetite, magnetite, garnet-andradite, pyrite, chalcopyrite, etc. Besides that, Fe in less amount is found in epidote, chlorite, hornblende, biotite, pyroxenes and other minerals. Some of these minerals are stable and preserve well during weathering. The other minerals can be easily disintegrated due to erosional processes that bring to transition of iron into a dissolved form. Fast oxidation of Fe in the river waters enables the formation of thin ferric suspension, which is transported to the sedimentary basins. Study of Kura and Terek rivers waters shows that 99.5–99.9% of Fe occur in the suspended form, and enter the Caspian Sea as the thin muddy flakes.

Unlike the Fe the biggest portion of manganese, nickel, cobalt, molybdenum, copper, zinc, lead usually is concentrated in the mica, amphiboles, feldspars, sulfide hydrates. These minerals during weathering processes are disintegrated quite fast. As a result the considerable part of elements contained in these minerals is released and transferred into solution. In the Caspian rivers (Volga, Ural, Kura, Terek) in the form of dissolved components migrate on average 0.25% of Fe; 1.7% of Mn; 23% of Ni and 33.7% of Cu.

Chrome is element of stable in the hypergenesis zone minerals such as chrome spinel (chromepikotite), chrome-containing mica. It is characterized by extremely low mobility and migrate in with the terrigenous particles containing chrome rich minerals.

Titan and vanadium are concentrated in magnetite, titanomagnetite, rutile, ilmenite. All these minerals are resistant to weathering that causes migration of these elements with clastic material.

Strontium and barium usually do not occur in the parent rocks in the form of their minerals. They are presented in the crystal lattice of calcite, plagioclases, potassium feldspars, augite, etc. These minerals are unstable in zone of hypergenesis. During weathering processes Sr and Ba are dissolved and can migrate in the form of bicarbonates, chlorides and sulphates in the water solutions. Quantity of Sr in the river water is $1.3x10^{-5}$ % on average, in the marine water – 1.3×10^{-2} %, i.e. river water is considerably depleted by Sr. If salts concentration in the marine water exceeds normal values for 4–5 times, the chemical accumulation of Sr in the form of Sr SO_4 (celestine) starts. This explains the lower proportion of Sr in sediments deposited in the fresh water environment, usually 0.01–0.02%. In terrigenous marine sediments the hight content of Sr is due to absorption by clay particles. This element also occurs in the crystal lattice of the shell aragonite.

In the sea basins barium ions supplied by river waters form a poorly dissolved mineral barite ($BaSO_4$). Barite is deposited and absorbed mainly in the near-shore sediments. In the sea water barium concentration is $5\times10\text{-}^{6}$% on average. Content of barium in the freshwater is significantly high – 1.7×10^{-4}%.

Different geochemical behavior of Ba and Sr allows using Sr to Ba ration to determine conditions of sedimentation: in the freshwater sediments it is lesser comparing with sediments accumulated in the marine environment.

From the plot summarizing data on the Sr / Ba ratio it is clear that 63% of the PS sandstones displays Sr / Ba ration values exceeding 1, while only 6.8% of mudstones are characterized by Sr / Ba >1 (from 1 to 1.51) (Figure 11). It means that sandy and muddy sediments were deposited in the different salinity regime, i.e. coarse-grained sediments were accumulated, mainly, in the marine environment with normal salinity, and mudstones – in from brackish to fresh water setting.

It should be mentioned that even we take the Sr / Ba ration equal to 0.56 that corresponds to average Sr / Ba ration in modern sediments of the Caspian Sea, no more than 12% of mudstones demonstrate this ratio exceeding the given threshold (Figure 12).

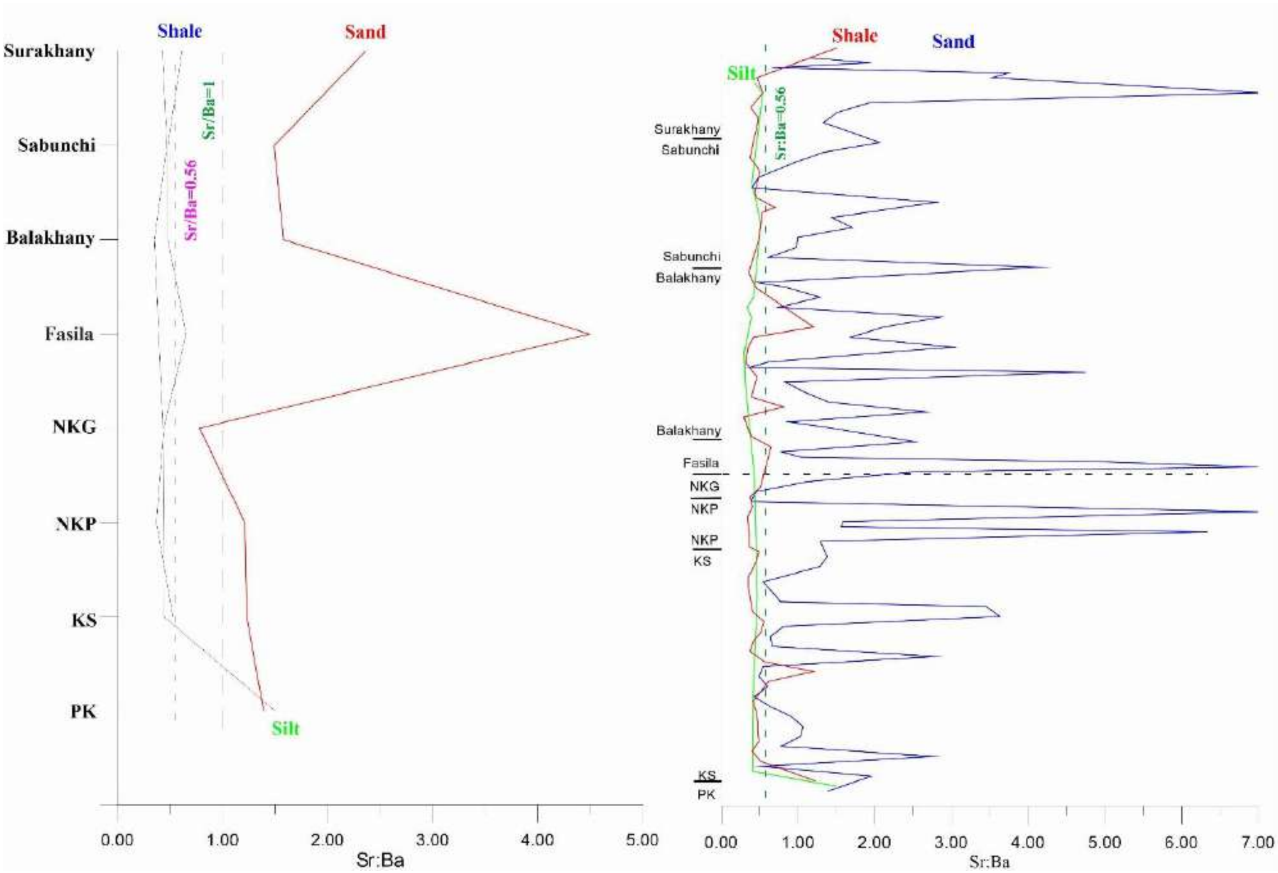

Figure 11. Average (**a**) and all (**b**) values of Sr / Ba ratio in the sandstones, siltstones shales of the different Productive Series suites exposed in the Kirmaki and Yasamal Valleys

In the low portion of PS the general trend of salinity decrease from the PK Suite to the NKG Suite is well pronounced. The NKG Suite sediments judging by Sr / Ba ratio both in shales and sandstones are dominated by freshwater conditions that are proved by micro faunistic studies of these deposits (Babazadeh, 2011). The foraminifera shells collected from the NKG Suite sediments are strongly stressed, that is manifested in their strong transparency and very small sizes.

Maximal salinity was recorded in the NKP Suite (Figure 11, 12).

In the upper portion of the Productive Series the most saline was the Fasila Suite basin during sand deposition (Figure11).

In Balakhany and Sabunchi time the salinity decreased, but didn't fall lower the normal sea salinity.

Below in the Table 4 we summarized the data on the maximal and minimal values of Sr / Ba ratio.

As it comes from the table 4 and Sr / Ba variations presented in the plots (Figure 11, 12) the most dramatic salinity variations occurred during accumulation of sediments of NKP, Fasila and Surakhany suites.

The lowest salinity is recorded for the NKG Suite basin.

Thus, the PS section represents a rhythmic alternation of freshwater-marine sediments that repeats with certain regularity. Based on the Sr / Ba ratio the 47 full cycles were distinguished. Taking the duration of the Productive Series equal to 2 Ma years, each such a cycle was continued for around 42 Ka years that corresponds to Milankovich cycles.

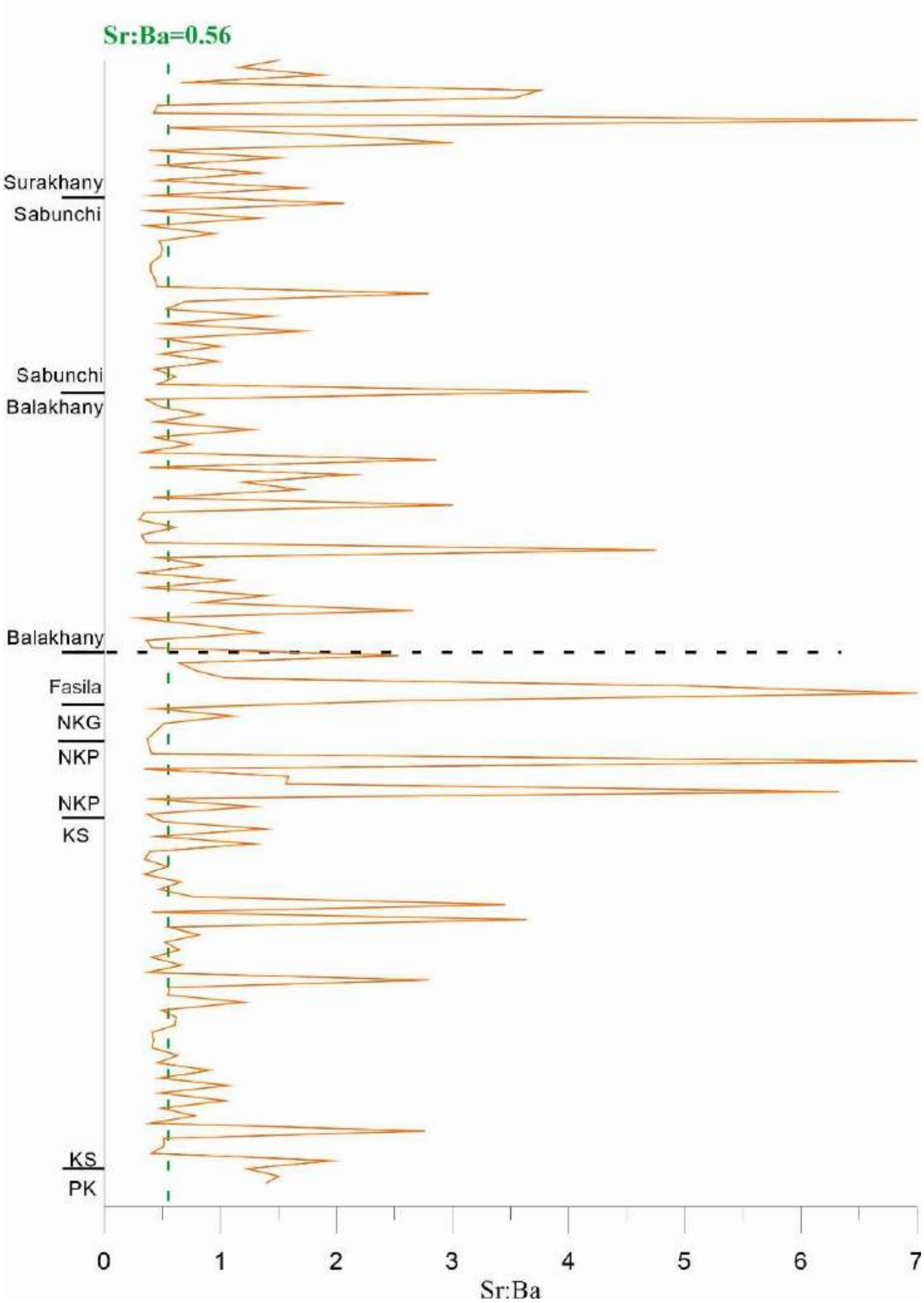

Figure 12. Sr / Ba ratio values variations in the Productive Series section, the Kirmaki and Yasamal Valleys

The Sr / Ba ratio indicate the sandstones accumulation in the saline environment, and muddy sediments – in the freshwater – brakishwater conditions. We explain it by increase evaporation during sand deposition that was accompanied by decrease of volume of water coming to basin resulted in the sea level fall. Water salinity reached high values that prevented mixing of river and sea water in the sand deposition sites dominated by deltaic facies. In contrast, during cooler periods the amount of fresh water running to the PaleoCaspain Sea was increasing, the sea water salinity decreasing, the sea level raising, and as a result, the studied locality was covered by distal sedimentation in the prodelta setting dominated by muddy sediments.

Table 4

Range of Sr / Ba variations in the various PS suite sediments

Suite	Shales			Siltstones			Sandstones			suite		
	Min.	Max.	Var.	Min.	Max.	Var.	Min.	Max.	Var.	Min.	Max.	Var.
Surakhany	0.38	1.51	1.13	0.43	0.54	0.17	0.66	35	34.34	0.38	35	34.62
Sabunchi	0.37	0.7	0.33	0.4	0.5	0.11	0.4	4.17	3.77	0.37	4.17	3.8
Balakhany	0.29	1.2	0.91	0.3	0.42	0.12	0.36	4.75	4.39	0.29	4.75	4.46
Fasila	0.65						0.79	15	14.21	0.29	15	14.71
NKG	0.37	0.51	0.14				0.45	1.11	0.66	0.37	1.11	0.74
NKP	0.34	0.4	0.06				0.38	24	23.62	0.34	24	23.66
Kirmaki	0.35	1.22	0.87	0.4	0.47	0.07	0.43	3.64	3.21	0.35	3.64	3.29
PK				1.5			1.3			1.39	1.5	0.11

Thus, studies of trace elements provide an opportunity for various paleoenvironmental reconstructions. For instance, knowing the element transportation mode promote our understanding of the basin facies zones. The migration of element in the form of solution brings the maximum of its accumulation to the muddy sediments of the pelagic zone. If element is transported by terrigenous particles, its maximal amount is recorded in the shoreface zone in the coarse-grained sediments.

If element migrates mainly as absorbed by colloid micelle, then its content values maximum falls to muddy rocks. But if the element is transported by terrigenous particles and occurs in the crystal lattice of minerals composing this clastic material, then the element maximum content can be recorded in the silty and sandy rocks.

Thus, the transportation mode and grain size are the basic factors affecting chemical elements distribution. As well as sediments are sorted the levels of element content in series sandstones-siltstones-shales are more contrasted; in the poorly sorted rocks distribution of elements is more smoothed. To describe patterns of elements distribution we used such parameter as an order factor (OF) that is a ratio of number of elements displaying graded content values from sandstones to siltstones and shales, to a total number of elements found in the sediments.

The smallest ration of OF equal to 0.416 is recorded in the sediments of the lower portion of PS - PK and NKG suites which testifies to poor differentiation of clastic material (Figure 13).

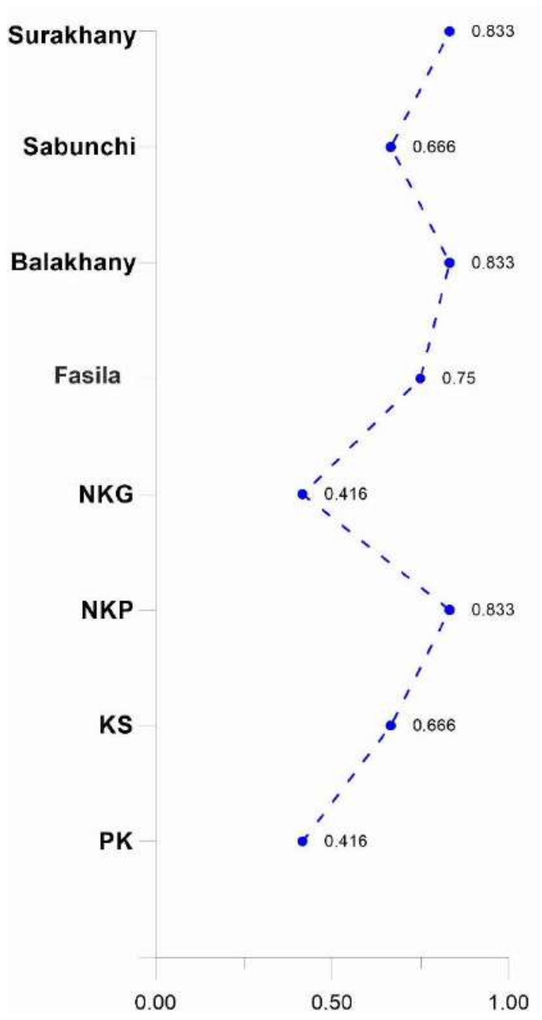

Figure 13. Order factor values in sediments of the Productive Series various suites exposed in the Kirmaki and Yasamal valleys

In the NKP Suite the maximal OF value equal to 0.833 is recorded that indicates the solution transportation mode (Figure 13).

In the upper section of PS the OF values are increasing from the Fasila Suite to the Surakhany Suite (Figure 13). It testifies to prevailing solution transportation mode in the upper suites of the Productive Series.

Trace element studies provide a good opportunity for reconstruction of paleoenvironmental characteristics such as salinity, depth and facies distribution in the paleobasins.

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CƏNUBİ XƏZƏR HÖVZƏSİNİN PLİOSEN ÇÖKÜNTÜLƏRİNİN MİKROELEMENTLƏRİNİN GEOKİMYASI

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Abşeron yarımadasında yerləşən Yasamal və Kirməki dərələrinin məhsuldar qatının çöküntülərində aşkar edilən mikroelementlərin tərkibinin öyrənilməsi nəticəsində sedimentasiya şəraitinin yenidən qurulmasının praktiki əhəmiyyət kəsb edən bir sıra göstəriciləri müəyyən edilmişdir. Stronsiumun bariuma nisbətinin tədqiqindən belə nəticə əldə edilmişdir ki, çöküntü toplanma hövzəsinin fasilə lay dəstəsi daha yüksək duzluluğa malikdir. Buna baxmayaraq Balaxanı və Suraxanı lay dəstələrinin çöküntüləri az duzlu su hövzəsində toplanmışdır. Məhsuldar qatın alt hissəsində Kirməkialtı lay dəstəsindən Kirməkiüstü gilli lay dəstəsinə doğru duzluluğun azalması müşahidə olunur.

Məhlul şəklində elementin miqrasiyası zamanı onun maksimal həddi dərinsulu zonanın gilli çöküntülərində həmçinin aşkar edilməmişdir. Əgər element qırıntılı hissəciklərlə daşınırsa, onun maksimum konsentrasiyası dayazsulu zonanın qumlu çöküntülərində baş verəcəkdir.

ГЕОХИМИЯ МИКРОЭЛЕМЕНТОВ ПЛИОЦЕНОВЫХ ОТЛОЖЕНИЙ, ЮЖНО-КАСПИЙСКИЙ БАССЕЙН

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На основе изучения микроэлементного состава отложений продуктивной толщи, обнажающихся в Кирмакинской и Ясамальской долинах, расположенных на Абшероснком полуострове, было выявлен ряд показателей, имеющих практическое значение при проведении реконструкции условий осадконакопления. Было показано по данным изучения отношения стронция к барию, что наибольшей соленостью обладал бассейн накопления отложений свиты перерыва. При этом отложения балаханской и сабунчинской свит накапливались в условиях солоноватоводного бассейна. В нижнем отделе продуктивной толщи отмечается тренд падения солености от подкирмакинской свиты к надкирмакинской глинистой свите.

Также, не было выявлено, что при миграции элемента в виде растворов его максимум отмечается в глинистых отложениях глубоководной зоны. Если элемент переносится обломочными частицами, максимальная концентрация его будет иметь место в песчанистых отложениях мелководной зоны.