# GEOCHEMISTRY OF LOWER AND MIDDLE JURASSIC DEPOSITS IN THE CENTRAL CAUCASUS

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The distribution characteristics of 19 chemical elements have been studied in the Lower and Middle Jurassic sandy—clayey deposits of the Labin-Malkinsk zone, at the southern margin of the epi-Hercynian Skifsk Platform. The role of various factors influencing concentrations or diffusion of elements have been investigated in continental (swamp, alluvial, etc.) and marine deposits, including the oolitic iron ore horizons.

Comparative studies of the behavior of chemical elements in sediments from various depositional facies and in units that accumulated in various structural—tectonic zones help in clarifying principles that govern concentration or diffusion of elements by depositional processes. We investigated Lower and Middle Jurassic terrigenous deposits of the Greater Caucasus. In the present paper, we discuss the geochemical characteristics of Jurassic rocks in the Labin-Malkinsk Zone (Central Caucasus). This is the southern margin of the epi-Hercynian Skifsk Platform. Several sections were studied in the eastern part of the Zone, including sections along the Baksan River, its left tributary, the Tyzyl River, the Dzigiat River, etc. Additional sections came from the right-bank of the Tyzyl River (Bardyrgrarlykol and Tashlysyrt Creeks) where relatively thin (c, 600-700 m) continental and marine sediment sequences occur.

The study area is 5-10 km north of the Tyrnyauz—Pshekishsk depression zone that separates the Greater Caucasus geosyncline from the Skifsk Platform.

Distribution of 19 elements and $CO_2$ (in carbonates) was studied in the Lower and Middle Jurassic beds. Fe, Mn, Ti, P, organic C, and $CO_2$ were analyzed by chemical methods; V, Cr, Co, Ni, Cu, Ga, Ge, Mo, and Pb by quantitative spectral analysis (79 samples), Zn, Zr, Rb, Y, and Nb by the x-ray fluorescence spectroscopy method (24 samples). Analyses of individual elements, total silicate analyses of clayey rocks, and carbonate rock analyses were carried out at the Chemistry Laboratory of the Geological Institute of the Academy of Sciences of the USSR.

## COMPOSITION OF THE LOWER AND MID-JURASSIC SECTION

The Mesozoic deposits in the Tyzyl River region overlie a thick sequence of Proterozoic and Paleozoic, dislocated schists, cut by pre-Jurassic granites, quartz porphyry and albite dikes and small ultrabasic intrusives. Small but numerous polymetallic ore occurrances are present in the crystalline schists, associated mostly with tectonic fractures [12]. The ores are pre-Jurassic in age and do not occur in Lower Jurassic deposits.

The Mesozoic sediments overlie the crystalline rocks with a sharp angular unconformity with a steady layering. They form a NE-dipping monocline. The absence of folding and any significant magmatism sharply contrasts these formations from geosynclinal rocks. The Lower and Middle Jurassic deposits north of the Tyrnyauz-Pshekish Zone thus are regarded as the lower structural substage of the Epihercynian platform mantle of the Skifsk Platform [13]. The sequence includes the Khumarinsk, Dzhigiatsk and Dzhorsk Formations (Fig. 1), and the locally developed Sarydyuz Formation.

The Khumarinsk Formation (Pliensbachian — Kariksian) [4] forms the basis of the Jurassic sequence and is 70 m thick. The formation starts with 10-15 m of argillites that fill the pre-Jurassic depressions. They pinch out horizontally. The argillites are mostly light gray and dark brown colored, platy layered. Layering is mostly indistinct; locally

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Geological Institute, Academy of Sciences of the USSR, Moscow. Translated from Litologiya i Poleznye Iskopaemye, No. 5, pp. 89-110, September-October, 1985. Original article submitted May 16, 1984.

 0024-4902/85/2005-0494$09.50 

layered plant detritus accumulations do occur. The bedding planes often carry leaf and stalk impressions. Few siderite concretion layers occur in the argillites. In thin (5-8 cm) layers, poorly sorted sandstones display numerous plant root traces.

The argillites are mostly composed of kaolinite, with illite admixtures.

A distinguishing feature of this part of the section is the presence of coal layers and lenses (5-10 cm), interlayered with coaly argillites. Pollen and spore analyses show (M. V. Azmaiparashvili and others) that the coal layers are composed of higher land plants (ferns and gymnosperms).

One of the sandy layers with root traces in its lower horizon displayed thin (7 cm) sulfide layers that were persistent horizontally. These contained mostly pyrite; also chalopyrite and galena mineralization [9]. The sulfide (pyrite) pockets also occur in the coal beds. In the septarian fractures galena, rarely sphalerite, occur in siderite concretions. The sulfide veins are displayed in quartzite pebbles; in disintegration products of the pre-Jurassic basement.

The relatively small thickness of the clay layer and its discontinuous character in horizontal direction, the abundance of plant fragments, root traces, coal layers, predominance of kaolinite among the clay minerals indicate a stagnant, lake—peaty swamp depositional facies.

The clay beds are covered by a complex, 5-10 m sequence of breccias, conglomerates, gritstones, sandstones, and rarely clayey siltstones; a whole spectrum of detrital rocks. These are not persistent horizontally and similarities even between relatively closely located sections (distances of a few hundred meters) are difficult to establish. Quartz pebbles dominate in the conglomerate and breccia layers; there are also sharply angular or poorly rounded crystalline schist fragments. The bedding planes between layers of different grain size often are uneven, with pockets intruding into the underlying beds. A bed of coarse pebble conglomerate (1.5 m) with coarse, unidirectional crossbedding that flattens out at the sole of the bed is also present. The cross-sets are 20-30 cm thick. In the sandy layers and in the cement of the conglomerate and breccia dark mineral concentrates are frequent. Occasionally, the rocks are stained by iron hydroxides. In the rare silty argillite layers, the bedding planes carry imprints of land plants. The coarse-detrital rocks are cemented by sandy—clayey matter; the sandstones by clayey, silica, occasionally, by carbonate cement.

We are in agreement with Karasev and Makarov [9] who mapped lithofacies in this area. The coarse detrital rocks in this sequences are regarded as colluvial—proluvial deposits of alluvial fans and sediment trains.

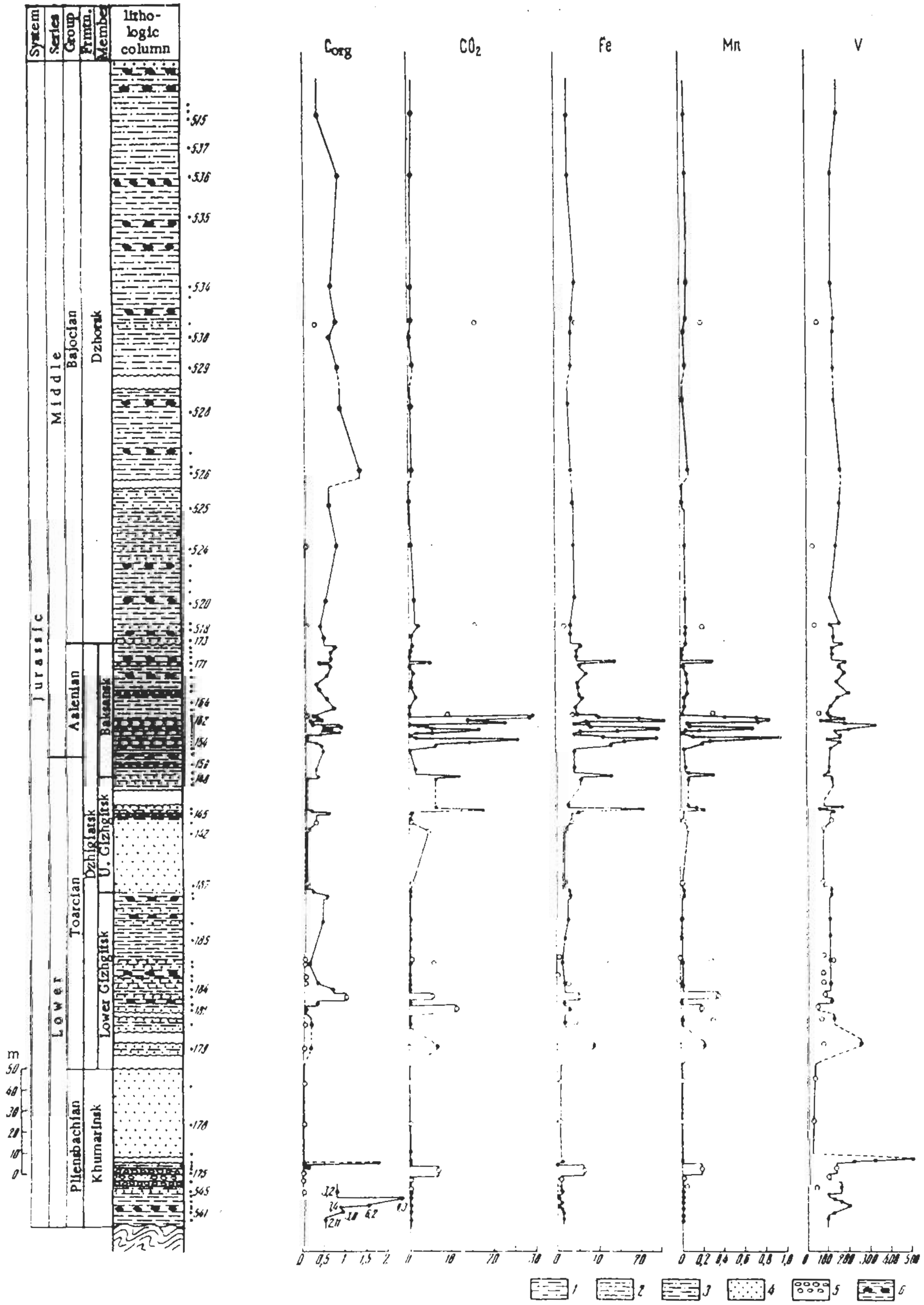
The upper part of the Khumarinsk Formation is represented by light-gray sandstones that are oligomictic with dominantly quartzitic composition. These are massive and 30-40 m thick. Thin (2-5 cm) lenticular layers and rare, maximum 0.5 m gritstone and small-pebbly conglomerate beds are rare and the bedding plane on their sole, uneven. Gravel fills the erosional pockets in the underlying sandy rocks. In the upper part of the sequence cross stratification was noted at various levels, with a dominant dip direction. Most sandstones are quite well sorted and only certain layers of several tens of cm thickness are enriched to a minor degree in clay matter. The rocks are composed of fine- and medium grained quartz sand in which feldspars play only a minor role.

Sandstones of this unit apparently formed in river channels in an alluvial setting. In certain views, given sand horizons of the Khumarinsk Formation were deltaic in origin [10].

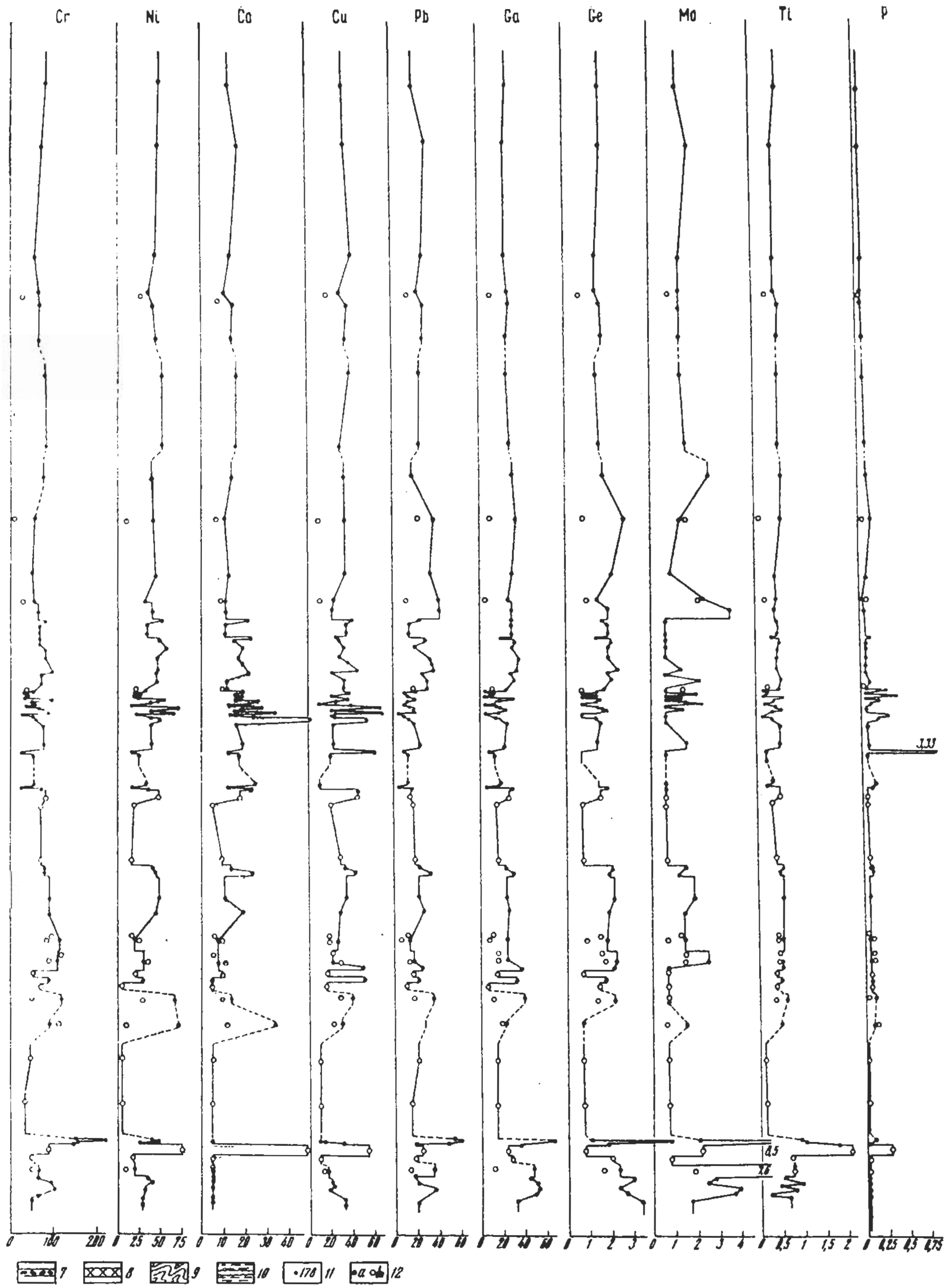
The continental deposits of the Khumarinsk Formation in the Tyzyl River basin contain very few fossils and the Pliensbachian (Kariksian) age is mostly based on comparison with other regions where units of the same age were deposited in marine environments, characterized by a much better defined fauna [14]. Although the Khumarinsk Formation in this section is thinner than further to the west (the upper part of the Formation was eroded), deposits of a variety of facies occur there. Deposits of the Dzhigiatsk Formation (Middle Toarcian-Aalenian) overlie the erosional unconformity over the Khumarinsk Formation [4]. Their fauna includes pelecypods, belemnites and ammonites, indicating marine conditions. A threefold subdivision is noted: Lower Gizhgiatsk (Middle Toarcian), Upper Gizhgiatsk (lower Upper Toarcian) and Baksansk (upper Upper Toarcian-Aalenian) beds.

The Lower Gizhgiatsk beds (80-90 m) are basically composed of interlayered, thin (few centimeters to few tens of centimeters thick) argillite, siltstone, and sandstone layers. In the lower part of the sequence beds of a few meters thickness alternate with each other.

Fig. 1. Lithological columnar section of Lower and Middle Jurassic deposits and element dis-
stones; 5) conglomerates; 6) concretions; 7) concretionary conglomerates; 8) iron-ore hori-
12) element composition in individual samples in the distribution curve: a) in clay rocks;
to scale. Figures show individual values in the samples. Concentration of organic C, $CO_2$,



tribution curves in the rocks. 1) Argillites; 2) silty argillites; 3) aleurolites; 4) sand-
zons; 9) pre-Jurassic basement rocks; 10) closed intervals; 11) sample location and number;
b) in sandstones. Distribution of organic C in argillites of the Khumarinsk Formation shown
Fe, Mn, Ti, and P shown in % in this and the next figure; other elements shown in $10^{-4}$%.



The clayey rocks include pure argillitic to essentially aleuritic types. The argillites are not distinctly layered and are gray to dark gray, sometimes with brownish hues. The aleurolites are massive, gray, nodular, locally quite clayey. Fine, carbonaceous plant detritus occurs on bedding plane surfaces. The sandstones are fine-grained, light gray, mostly oligomictic with feldspar and quartz content. Individual beds reach 3-4 m. The sandstone layers generally are horizontally persistant but thin layers (few centimeters) sometimes pinch out. The well-sorted sandstones are indistinctly layered. Bedding is visible only on weathering surfaces in instances when outlined by Fe-hydroxides. Distinct cross-bedding is visible only in rare, relatively thick beds in the lower part of the beds. Repeatedly, sediment weathering surfaces occur in sandstone beds with subsequent concentration of new units of sandy matter.

Siderite is common in these beds. In argillites and aleurites it forms concretions; in sandstones, zones of cementation.

Few faunal elements occur in these deposits. They are represented by marine organisms (ammonites, crinoid fragments, etc.).

Subaqueous erosion surfaces in the sandy beds and cross-bedding indicate relatively high energy conditions in the marine waters. Weak indications of wave action is typical in these deposits. Few representatives of benthic faunas, fine sand grain size, thin lamination in the sandy sequences all indicate that the sediments were deposited in a transitional zone between shallow and much deeper shelf facies belts.

The Upper Gizhgitsk beds (50-60 m) are composed of light gray, fine-grained sandstones with occasional greenish hues and intermediate density. Cross-lamination occasionally is displayed on the weathered surfaces. The different sets have different dip directions. Traces of erosion also occur; the erosional depressions are also sand-filled. Quartz and feldspar, with mica, occasionally, carbonate cement form the sandstones.

This sequence also includes a few gray siltsone layers, sometimes alternating with 1-3-cm-thick sand units. Siderite concretion occur in the siltsones. Erosion of the concretion-bearing siltstones resulted in formation of two 0.15-0.3-m-thick beds of iron-oolitic concretion conglomerates without the presence of a carbonate-clay cement throughout the total rock unit. An abundance of marine fauna occurs in these beds: belemnites, ammonites, pelecypods, crinoid fragments, etc. In the upper half of the Upper Gizhgitsk beds, a sand bed with plant root traces underlies one of the concretion conglomerate beds. Nearer to the roof of the bed, sorting decreases in the rock. Clay appears in the sandstones and renders them layered, with tabular bedding structure.

The deposits formed in shallow seawater, with higher wave energies. The sandy matter formed in banks. These underwater shoals occasionally developed plant growths.

The Baksansk beds (60-65 m) are represented essentially of siltsones, containing numerous concretion-bearing layers, with concretion conglomerates and oolitic ironstones. In contrast with adjacent areas in this section, the upper Baksansk units did not form due to erosion that preceded accumulation of the overlying Dzhorsk Formation [4].

The argillites are dark gray, sometimes with greenish hue. Layering is absent or poorly displayed. Siltstone varieties abound. The bedding plane surfaces carry traces of crawling organisms. Numerous concretion conglomerate beds (10-30 cm) are typical in the unit but not persistent horizontally. The total thickness of this interval is 1-3 m. The argillites include a few thin (2-4 cm), lenticular beds or organic greenish gray limestones. In the upper half of the sequence, lenses and thin sandstone layers (2-3 cm) occur. They are gray, fine-grained, locally cross-laminated. As the argillites, the sandstones also contain fine pyrite impregnations.

Iron oolites layers distinguish the Aalenian beds from the rest of the Jurassic sequence. In addition to the four thickest beds (70-200 cm), there are a few thin (10-20 cm) beds. Oolites also occur in the concretion conglomerate cement. The oolite beds are denser than the enclosing argillites and are sharply outlined in the topographic relief. The beds are heterogeneous and the component layers differ in hardness and color that ranges from dark greenish gray to reddish brown. The groundmass contains small (few centimeters) concretions of irregular orientation, belemnite and ammonite fragments, and bivalve detritus. Most layers have a brecciated structure.

The oolites are unevenly distributed in the rock. In certain portions, they form a continuous oolite mass, in others there are only few oolites present. The oolites are round or oval-shaped, 0.4-0.6 mm; sometimes maximum 1.0 mm in size. Commonly they are reddish brown, with a concentric structure. Aggregates of 2-3 individual oolites, enclosed by a common envelope, also occur. Most oolites are composed of goethite and hydrogoethite. Chamosite-bearing varieties are rare and are partially replaced by calcite. The cementing agent is mostly clayey—carbonate siderite—calcite matter. Deficiency in carbonate cement is proportionally accompanies by an increased degree oolite deformation, fracturing and flattening. Shell and crinoid fragments may also be enclosed in an iron envelope. Porous fragments and carbonate cement are impregnated by reddish brown iron hydroxides. Certain oolites are partially replaced by pyrite.

Oolites also occur in argillites (basically at the interstratified interval of oolitic beds) but there are few of them, are crushed and occur in fragments.

The Baksansk beds are characterized by horizons of repeated reworking, the absence of sharply defined layering in argillites as the result of constant sediment resuspension. Cross-lamination occurs in the sand lenses, brecciation of the oolite-bearing beds. Traces of bottom-dwelling organisms and other features suggest that the sediments accumulated in relatively high energy, shallow marine conditions.

The *Dzhorsk Formation* (Bajocian), as regional studies have shown, overlies the preceding deposits with an erosional unconformity [4]. The lower portion of the formation consists of gray and dark-gray silty argillites, transitional toward clayey siltstones. Sideritic concretions and large (maximum few meters in diameter) limestone lenses, sometimes with siderite concretions, occur 50 m above the base of the Formation a 40-m unit of interlayered sandstone (25-120 cm) gray silty clay (1-2 m) layers occurs. The sandstones are mostly fine-grained, feldspar and quartz-bearing, massive (nonlayered), or with poorly developed thin layering. Locally, flat cross-layering or wavy bedding do occur. Plant detritus occurs on the bedding planes, with rare plant fragment impressions. The lower bedding planes occasionally carry sole marks, indicators of bottom currents.

In the upper part of the Dzhorsk Formation argillites occur with various amount of silt content. There are practically no clean varieties. Siltstones are of minor importance. Thin (10 cm) sandy—siltstone beds, often with calcite and siderite cement, also occur. Several-meter-thick concretion beds are also present. Bioturbation occurs in a few sediment horizons. The formation varies in thickness; in the study area it is c. 270-300 m thick.

Various indicators suggest that these sediments formed in the open sea, at some distance from shore. In the beginning, this was a relatively shallow water-setting that deepended later to become a deeper shelf facies.

The Middle Jurassic section is capped by silty—sandy beds, few tens of meters thick, with large amounts of plant detritus, dispersed in the rock, with a few centimeters of thin coal layers. Cross lamination is noted in the sandstones. Numerous lenses and layers of siderite nodules provide a banded appearance in certain beds. As in the Pliensbachian coal deposits, a a thin (10 cm) layer occurs, with sulfide impregnations. It contains pyrite, with galena and sphalerite admixture. This bed (Sarydyuz Formation) is considered to be a coal-bearing continental unit. Its age, based on the stratigraphic position, is thought to be Bathonian [4].

The accumulation of the Lower and Middle Jurassic deposits occurred from several source areas of terrigenous sediments. This is shown particularly by the various accessory mineral spectra. Bezborodov [3] indicated that the heavy mineral composition of the Toarcian sandy—silty rocks is relatively uniform. The sphene—rutile—tourmaline—zircon assemblage predominates. In the Tyzyl River area, sphene and other Ti-bearing minerals are typical, while garnets are absent. Higher in the section, the chlorite fraction increases. In the Aalenian deposits, the heavy mineral spectra are similar to those of the Toarcian. Sphene, rutile, tourmaline, zircon, and chlorite associations predominate. In the Bajocian beds the mineral spectrum is slightly different: zircon, chlorite, biotite, and garnet are present.

## ELEMENT DISTRIBUTION IN DEPOSITS OF VARIOUS FORMATIONS

The element distribution throughout the section is indicated by Fig. 1. The average concentrations of element, based on 76 sample analyses from various stratigraphic intervals are shown in Table 1. Certain elements were analyzed in a smaller number of samples (Table 2). Tables 1 and 2 show element concentrations in argillites of the Khumarinsk, Dzhigiatsk, and

TABLE 1. Element Distribution in Lower and Middle Jurassic Units

| Formation (member, bed) from which sample was taken | $C_{org}$ | $CO_2$ | Fe | Mn | Ti | P | Cr | Ni | V | Cu | Co | Pb | Ga | Ge | Mo | No. of samples | Rock types |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Khumarinsk Formation: argillite member | 4,67 | 0,08 | 0,87 | 0,003 | 0,68 | 0,003 | 83 | 31 | 149 | 27 | <10 | 27 | 46 | 2,7 | 3,7 | 6 | Argillites |
| conglomerate-gritstone-sandstone | 1,87 | None | 1,11 | None | 0,93 | 0,01 | 220 | 38 | 500 | 63 | <10 | 60 | 67 | 4,8 | 0,5 | 1 | » |
| | None | 7,00 | 6,75 | 0,18 | 2,12 | 0,26 | 88 | 76 | 142 | 54 | 53 | 24 | 23 | 1,5 | 2,2 | 1 | Sandstones |
| | » | None | 1,15 | None | 0,69 | 0,004 | 50 | 18 | 100 | <13 | <10 | 18 | 27 | 2,0 | 1,5 | 1 | » |
| member of alluvial sandstones | » | » | 1,12 | » | 0,13 | 0,006 | 37 | <10 | 35 | <13 | <10 | 18 | 14 | <1,5 | 1,5 | 3 | » |
| Dzhigiatsk Formation: Lower Gizhgitsk beds | 0,39 | 0,05 | 2,68 | 0,02 | 0,56 | 0,006 | 90 | 47 | 119 | 40 | 16 | 28 | 31 | 2,2 | <1,5 | 5 | Argillites |
| | 0,25 | None | 1,75 | 0,01 | 0,51 | 0,05 | 102 | 35 | 120 | 40 | 12 | 22 | 28 | 2,0 | 1,6 | 3 | Silty argillites |
| | None | 0,18 | 0,98 | 0,01 | 0,49 | 0,06 | 98 | 17 | 77 | 26 | 9 | 18 | 15 | 1,5 | <1,5 | 5 | Fine-grained sandstones and siltstones |
| | 0,26 | 9,84 | 7,26 | 0,33 | 0,49 | 0,053 | 107 | 28 | 94 | 27 | 11 | 15 | 13 | <1,5 | <1,5 | 4 | Fine-grained sandstones and siltstones with carbonate cement |
| Upper Gizhgitsk beds | None | 2,4 | 2,09 | 0,05 | 0,39 | 0,05 | 73 | 18 | 84 | 26 | 8 | 18 | 15 | 1,5 | <1,5 | 2 | Sandstones |
| | 0,4 | 0,22 | 4,46 | 0,04 | 0,53 | 0,04 | 78 | 42 | 125 | 36 | 20 | 15 | 27 | 1,75 | <1,5 | 2 | Clayey siltstones |
| | 0,31 | 6,25 | 24,58 | 0,19 | 0,38 | 0,15 | 70 | 33 | 198 | 28 | 29 | 14 | 21 | 1,75 | <1,5 | 1 | Siltstone with carbonate-iron cement and oolites |
| Dzhigiatsk Formation: Baksansk beds | 0,03 | 6,25 | 7,00 | 0,09 | 0,42 | 0,06 | 68 | 31 | 146 | 23 | 21 | 14 | 15 | <1,5 | <1,5 | 1 | Siltstone with carbonate cement |
| | 0,52 | 12,46 | 28,29 | 0,77 | 0,44 | 0,25 | 79 | 56 | 262 | 45 | 34 | 19 | 15 | <1,5 | <1,5 | 11 | Rocks, enriched in Fe(Fe >10%) |
| | 0,47 | 0,57 | 5,59 | 0,04 | 0,51 | 0,05 | 76 | 46 | 144 | 34 | 18 | 24 | 28 | 1,89 | 1,5 | 15 | Argillites |
| Dzhorsk Formation | 0,69 | 0,54 | 3,95 | 0,04 | 0,54 | 0,05 | 68 | 44 | 132 | 33 | 15 | 29 | 27 | 1,8 | 1,71 | 12 | Argillites with differing degrees of silt |
| | 0,2 | 13,17 | 4,16 | 0,27 | 0,3 | 0,06 | 35 | 27 | 58 | 21 | 10 | 25 | 14 | 1,5 | 2,78 | 3 | Fine-grained sandstones and siltstones with carbonate cement |
| Marine argillite deposits | 0,54 | — | 4,52 | 0,037 | 0,53 | 0,52 | 75 | 46 | 136 | 34 | 16 | 27 | 28 | 1,9 | 1,71 | | |
| Concentration coefficients of elements in continental argillites | 8,6 | — | 0,19 | 0,08 | 1,28 | 0,058 | 1,11 | 0,67 | 1,1 | 0,79 | 0,63 | 1 | 1,64 | 1,42 | 2,5 | | |
| Clarke values of elements in argillites. Based on Vinogradova [6] and Turekian and Wedepohl [28]. | 1,0 | — | 3,33 | 0,067 | 0,45 | 0,077 | 100 | 95 | 130 | 57 | 20 | 20 | 30 | 2 | 2 | | |
| | — | — | 4,72 | 0,85 | 0,46 | 0,07 | 98 | 68 | 130 | 45 | 19 | 20 | 19 | 1,6 | 2,6 | | |

Note. The table shows mean element concentrations of rocks in various stratigraphic intervals and element concentrations in certain individual samples; $C_{org}$, $CO_2$, Fe, Mn, Ti and P content given in %, rest: in $10^{-4}$%.

Dzhorsk Formation for a quantitative evaluation of the geochemical characteristics of continental and marine clayey rock. Calculation of marine argillites involved analyses of 32 samples. For comparison, the tables indicate clarke values, given by Vinogradov [6] and Turekian and Wedepohl [28].

Deposits of the *Khumarinsk* Formation, characterized by continental sediment accumulation in the region, displayed certain specific features of element distribution. The clayey sequence of lacustrine—swampy deposits at the base of the Formation is distinguished sharply within the Middle- and Lower-Jurassic sequence by its organic content. Organic carbon ranges between 2.9-9.3% (4.6% on the average). Calculation of concentration ratios in the argillites of the Formation* indicated (Tables 1 and 2) that the organic carbon is eight times more abundant in them than in rocks of the rest of the section. The abundance of carbonized plant remains in the Formation (primarily in the argillites) is shown by the organic matter composition: humin compounds abound, while bituminous compounds are insignificant [3]. Argillites in this unit also contain increased concentrations of Ti, Ga, Ge, Mo, Zr, Rb, Y and Nb; although their concentration coefficients are smaller and only in Mo and Nb do exceed the value of 2.

There is also an element group with small concentration values in argillites of the Khumarinsk Formation. It includes primarily Fe, Mn, and P (Fig. 1, Tables 1 and 2). The Fe concentration is everywhere less than 1.5%. It decreases to 0.42%, even to 0.1% (the average Fe content is one-fifth of the clarke value). In most samples, Mn was absent or present only in minimal amounts; P was practically absent. Co, Ni, Zn, and Cu(?) belong to the same group. These are elements with geochemical characteristics, close to those of Fe.

V, Cr, and Pb represent a group with concentration coefficients close to 1; they did not accumulate or disperse in the Khumarinsk argillites. In a thin (30 cm) argillite bed in the conglomerate and gritstone sequence, V, Cr, and Pb displayed high concentrations (Table 1), similar to those of the first element group.

Evaluation of the composition of the basic rock-forming components in clayey rocks (Table 3) indicates that the Khumarinsk argillites typically display higher values of $Al_2O_3$ and lower values of $SiO_2$, MgO, $Na_2O$, and $K_2O$. Ferric oxide showed a sharp decrease, in contrast with ferrous oxide.

In rock units with coarse-grained composition and various stages of sorting (conglomerates, gritstones, and sandstones) that overlie argillites, the element concentrations are quite varied. Beds with low concentrations alternate with beds in which high concentrations of certain elements (Fe, Ti; Fig. 1, Table 1). This resulted from uneven distribution of dark ore minerals in the rocks. The next unit upward in the sequence, composed of fine-grained alluvial sandstones, is characterized by, on the other hand to tally uniform element distribution. The concentrations are the lowest in the whole section and uniform throughout the entire unit.

*Dzhigiatsk Formation,* Lower Gizhgitsk Beds. As this unit is composed of essentially of interstratified argillites, siltstones, and sandstones, the element distribution curves (Fig. 1) display intricate patterns. The relatively low fe and Mg concentrations (2.68 and 0.02%, respectively) in argillites and in silty argillites (1.75 and 0.01%, respectively; Table 1) should be noted. In addition, in certain beds, aleurolites and fine-grained sandstones are thoroughly or just locally cemented by siderite. The Fe and Mn concentrations (7.26, respectively 0.33%) are many times higher in them than in sandstones of carbonate-free cement (0.98 respectively 0.01%).

In the Lower Gizhgitsk sandstones, in contrast with alluvial sandstones of the Khumarinsk Formation, the Ti, P, Cr, V, and Cu concentrations are high. The Ti, P, and Cr-content is similar to that found in clayey rocks. Zr behaves differently: its concentration increased greatly to maximum values found in fine-grained sandstones ($463 \cdot 10^{-4}$%; Table 2). The distribution of the remaining elements follows regular patterns: higher in the argillites than in the sandstones.

*The concentration ratios express the relationship between element concentration in Khumarinsk argillites and their concentration in the Dzhigiatsk and Dzhorsk argillites.

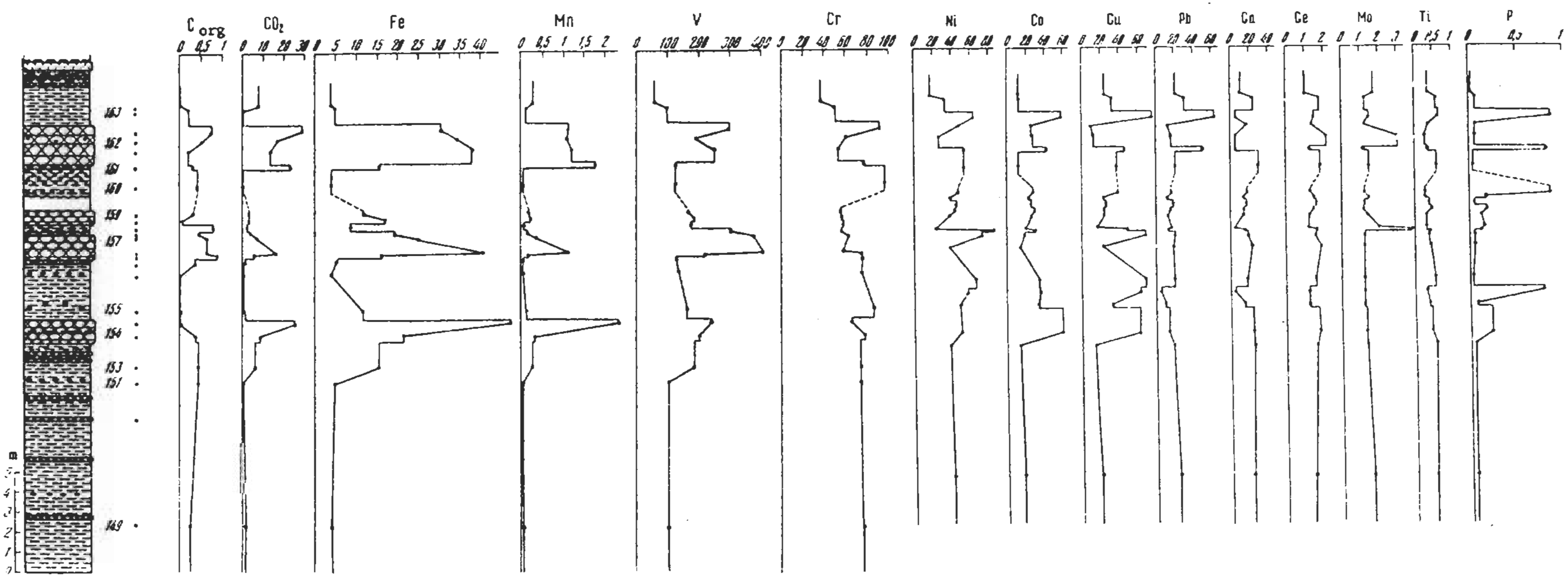



Fig. 2. Lithological column of lower part of the Aalenian sequence and element distribution in rocks. Symbols as in Fig. 1.

TABLE 2. Element Concentration in Lower and Middle Jurassic Rocks, in $10^{-4}$%

| Formation (member, bed) from which sample was taken | Zn | Zr | Rb | Y | Nb | Sample No. | Rock |
|---|---|---|---|---|---|---|---|
| Khumarinsk Formation: | | | | | | | |
| argillite member | 62 | 289 | 164 | 51 | 31 | 3 | Argillites |
| conglomerate-sandstone member | 45 | 179 | 65 | 41 | 20 | 2 | Sandstones |
| alluvial sandstone member | 30 | 40,9 | 19 | 10 | 5 | 1 | » |
| Dzhigiatsk Formation: | | | | | | | |
| Lower Dzhigiatsk beds | 122 | 205 | 136 | 38 | 16 | 2 | Argillites |
| | | 463 | 59 | 31 | 5.6 | 3 | Sandstones |
| Upper Dzhigiatsk beds | 61 | 432 | 66 | 31 | 12 | 2 | » |
| Baksansk beds | 109 | 192 | 116 | 30 | 13 | 4 | Argillites |
| Dzhorsk Formation | 107 | 182 | 113 | 35 | 13 | 5 | » |
| | 43 | 48 | 65 | 17 | 5 | 1 | Sandstones |
| | 117 | 92 | 56 | 25 | 5 | 1 | Siltstones with carbonate cement |
| marine argillites | 110 | 190 | 118 | 34 | 14 | — | — |
| Element concn. coeff. in argillites of continental deposits | 0,57 | 1,52 | 1,38 | 1,51 | 2.19 | | |
| Clarke of elements in argillites according to Vinogradov [6] and | 80 | 200 | 200 | 30 | 20 | | |
| Turekian and Wedepohl [28] | 95 | 160 | 140 | 26 | 11 | | |

A mostly low element concentration is typical of the Upper Gizhgitsk beds, composed dominantly of feldspar—quartz-bearing sandstones. As in the Lower Gizhgitsk beds, their concentration is much higher than in the Khumarinsk alluvial deposits. A high Zr value ($432 \cdot 10^{-4}$%; Table 2) was recorded in these sandstones.

In the Upper Gizhgitsk sequence, carbonate and clay beds appear with iron oolites that enclosed reworked concretions. Fe displayed much higher values (maximum 25%) in the carbonate—clay unit, as did other elements: Mn: 0.19%, P: 0.15%, V: $198 \cdot 10^{-4}$%, and Co: $29 \cdot 10^{-4}$% (Table 1).

The *Baksansk* beds contain iron oolite-bearing units and therefore display a sharp contrast toward the rest of the Jurassic units (Fig. 1). Because these horizons have a higher carbonate content ($CO_2$ reaches 30%), Fig. 2 gives element distribution values for this interval recalculated for a carbonate-free composition by use of a larger scale.

The oolite beds have higher (28% on the average) iron content (Table 1). Iron, therefore, is one of the leading rock-forming components. Figure 2 shows that the Fe-distribution is uneven in the beds, in conformity with their heterogeneous composition and the haphazard oolite distribution in the rock. Fe is primarily present in hydrogoethite, goethite, siderite, chamosite, and amorphous iron hydroxide compounds. Sulfide minerals play no important role in the mineralogy. The high Fe concentration plays a big role in defining the geochemical characteristics of these beds. Other elements also display higher values (Fig. 2, Table 1), above all: Mn(0.77%) and P(0.25%). To a lesser extent but still importantly, the V content also increased. Its distribution curve totally follows that of Fe. Figure 3 indicates the behavior of elements enclosed in rocks that are transitional between argillites and oolite beds. Oolitic concentrations coefficients are shown as CC. The CC-values of V and Co are close and the Cu and Ni CC-values somewhat low. Individual analyses indicate that cerium has higher values in oolitic beds ($90\text{-}120 \cdot 10^{-4}$%), in contrast with its value in the enclosing argillites ($54 \cdot 10^{-4}$%). Other elements (Ti, Pb, and Cr) show slight reaction to the iron enrichment in the rocks and Ge and Ga decreased in value (Table 1). Thin (few tens of centimeters thick) clayey—carbonate layers with oolite content and the cement in concretion conglomerate beds are not represented by element distribution curves, but geochemically are similar to the thick beds.

Argillites in the Baksansk beds contain no geochemical anomalies. Comparison of element concentration in them with average values in marine clayey deposits (Table 1) indicates simi-

TABLE 3. Chemical Composition of Clay Rocks of Lower and Middle Jurassic Deposits, in %

| Formation (member, bed) | Sample No. | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | FeO | MnO | CaO | MgO | $Na_2O$ | $K_2O$ | $H_2O^+$ | $H_2O^-$ | $CO_2$ | C | $P_2O_5$ | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Khumarinsk Formation | 541 | 52,04 | 1,11 | 25,88 | 0,31 | 1,77 | None | 0,74 | 0,66 | 0,22 | 2,90 | 6,11 | 0,78 | None | 4,25 | Traces | 100,07 |
| Dzigiatsk Formation | | | | | | | | | | | | | | | | | |
| Lower Gizhgitsk beds | 186 | 55,98 | 0,99 | 20,91 | 5,87 | 1,12 | 0,04 | 0,79 | 2,20 | 0,77 | 3,80 | 5,72 | 1,41 | » | 0,79 | 0,11 | 100,50 |
| Baksansk beds | 160 | 55,04 | 1,29 | 21,62 | 4,14 | 3,02 | 0,07 | 1,40 | 2,02 | 0,68 | 3,02 | 6,28 | 1,37 | » | 0,36 | 0,05 | 100,36 |
| Dzhorsk Formation | 536 | 63,91 | 0,74 | 16,62 | 1,24 | 3,00 | 0,04 | 1,89 | 1,56 | 1,35 | 3,78 | 3,03 | 0,58 | 0,45 | 0,46 | 0,09 | 99,97 |

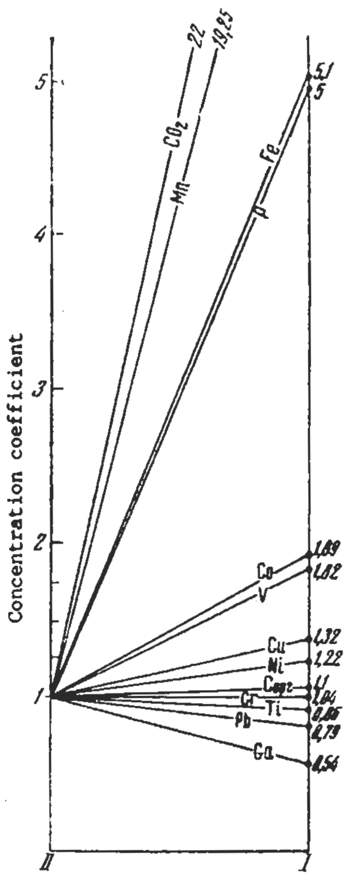



Fig. 3. Element concentration coefficient diagram in the iron ore horizons(I), in relation to the enclosing argillite(II).

lar values. Slight increase in the iron value (5.59%) is not accompanied by other element concentration changes. Rock-forming components in the Baksinsk argillites display similar values as argillites of other parts of the Dzhigiatsk Formation do (Table 3).

In contrast with lower units, the *Dzhorsk Formation* have a uniform element distribution (Fig. 1). In the marine deposits (Tables 1 and 2) the average element values are very similar to those of the clayey rocks in the Formation. Only Mo displayed a relative concentration increase. The argillites often contain silty quartz mixture, reflected by increased $SiO_2$ content in the rock (Table 3, Sample 536) and corresponding decrease in the other elements.

Thin (few centimeters and few tens of centimeters) sandy beds display an increase in the carbonate content, in contrast with the enclosing argillites (Table 1). Calcite and siderite cement formed. The Fe and Mn content, as well as the relative Mo concentration also increases in conjunction with this. Other elements in the sandstones have lower concentrations than in the argillites.

## DEVELOPMENT CONDITIONS OF THE GEOCHEMICAL CHARACTERISTICS IN THE ROCKS

Differences in formation conditions of various Lower and Middle Jurassic units have, to a significant extent, determined the element distribution patterns in the section. While in certain instances the accumulation and burial of sediments was not accompanied by significant reworking and the sediments essentially inherited the composition of the source sediments, in other cases the geochemical aspects of the rocks were determined by postdepositional processes.

The element distribution in the Khumarinsk Formation was determined by a complex of several factors. As shown before, argillites at the base of the sequence have an anomalously high organic C-content, related to the accumulation and burial of plant matter in swamps and plantclogged lakes. Fe, Mn, P, and $CO_2$ accumulated in minimal concentrations. However, initially, before diagenetic element redistribution started, the concentration of these elements shows a different pattern in the sediments. This is shown by the fact, for instance, that in coeval sediments of other sections, clay beds did not accumulate in stagnant water basins with very minor amounts of organic C, in which diagenetic processes were slow. Redistribution of sediment components did not take place to any extent under such circumstances; the corresponding Fe, Mn, and P values are close to clarke concentrations.

In lacustrine—swamp deposits, the abundance of reacting organic matter caused intensive diagenetic reorganization of the sediment matter. Disintegration of the organic matter, reduction of oxidized forms of Fe and Mn, and their transition to highly mobile bicarbonate forms represented a prerequisite for the reorganization. However, if reorganization involved only Fe, adsorbed by clay matter and incorporated also into separate hydroxide particles, the iron concentration would not decline to minimal values. Apparently, in sediments of the Pliensbachian continental water basins unusual conditions resulted in the presently recorded patterns. It is known, for instance, that in many modern swamps and lakes the muddy waters are acidic [11]. The discussed sediments are believed to have accumulated under similar conditions. As a result, a large portion of the Fe-bearing silicate minerals were dissolved, with release of iron and other cations. These elements were redistributed in the sediments and gravitated to concretions, or were differentiated in the bottom waters, or were diffused in waters above the bottom that emanated from the sediment. Table 3 shows that (sample 541), in addition to low Fe, Mn, P, and $CO_2$ content, argillites at the base of the section also have low concentrations of CaO, MnO, and $Na_2O$. Vigorous emission of cations from the sediment during diagenesis result predominantly in authigenic kaolinite formation. This mineral is accompanied only by illite admixture in the rock.

Destruction of terrigenous components during diagenesis in the sediment is proven by the study of Quaternary sediments. The dynamics of clay mineral alteration in modern peats in the Rioni intermontane basin were studied in detail by Timofeev and Bogolyubova [5, 16]. They have shown that during peat diagenesis in acidic medium a gradual diminution of montmorillonite and chlorite content takes place in the buried sediments. At the same time, the kaolinite content increases and sometimes free silica forms during silicate mineral decomposition. At the release of Fe and Mg from the minerals during dissolution, the elements become soluble and enrich the muddy waters.

In the Pliensbachian deposits, the fate of Fe, Mg, Ca, and Mg depended on characteristics of the water basin, and in particular on the carbonic acid saturation of the bottom and muddy waters. If the change of carbonic acid concentration with changing depth was significant in the sediment, $FeCO_3$ settled and Ca, Mg, and Mn were isomorphically substituted in it in the near-surface mud horizons. Carbonate layers and concretions formed, as the result (Table 4, sample 539) [7]. If the sediment bottom water did not allow bicarbonate diffusion, then bicarbonates left the mud and were dissolved. Thus, in a given set of conditions clay sediments were depleted in certain components.

The behavior of certain elements in organic matter-enriched sediments indicated that they are caused to enter into metalloorganic compounds. It was shown that Fe, Mn, Co, Ni, Mo, Cu, Pb, Zn, V, and Ag form compounds with humates (Swanson et al.) [26]. Most of these elements form a group that has lower concentrations in the Khumarinsk Formation argillites. Their redistribution in the sediments led to formation of water-soluble metalloorganic compounds.

A number of elements (Ga, Ge, Mo, Ti, Zr, Rb, Y, and Nb) have relatively higher concentrations. Apparently, some of them are linked with the enrichment of the rock by organic plant matter; although of these only Ge has the tendency to concentrate in the coal layers ($5\text{-}7 \cdot 10^{-4}\%$). No clear answers exist as to what forms other elements take. Argillites contain silty admixture that include feldspar, accessory, and other ore mineral grains. However, there is little silty matter in the rocks and it is unlikely that it would have any influence on element concentrations. We believe that silty matter originally was more abundant but under specific conditions of the Pliensbachian continental water basins, under the influence of aggressive muddy waters the mineral grains were dissolved. Corrosion and solution marks are common on mineral grains. Certain components of the destroyed minerals entered bottom waters, others, including elements of the discussed group, were attached to the sediment through sorbtion on clay particles or organic matter. They may also have formed microprecipitates of new authigenic minerals.

TABLE 4. Chemical Composition of Carbonate Concretions, in %

| Formation (member, bed) from which sample was taken | Sample No. | MHO* | $Al_2O_3$ | $Fe_2O_3$ | FeO | MnO | CaO | MgO | $CO_2$ | $C_{org}$ | $P_2O_5$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Khumarinsk Formation | 539 | 34,21 | None | 2,21 | 32,12 | 1,02 | 2,12 | 2,73 | 23,65 | 0,46 | 0,24 |
| Dzhigiatsk Formation: Lower Gizhgitsk beds | 182 | 12,20 | » | 3,18 | 40,10 | 0,91 | 2,51 | 7,71 | 32,10 | None | 2,23 |
| Baksansk beds | 151 | 24,56 | » | 5,20 | 7,27 | 0,04 | 20,54 | 2,85 | 20,20 | 0,22 | 7,23 |
| | 155 | 17,50 | 1,48 | 5,19 | 12,97 | 0,09 | 19,49 | 1,79 | 19,45 | 0,19 | 6,90 |
| | 160 | 12,91 | None | 2,39 | 31,44 | 1,41 | 12,86 | 3,55 | 24,75 | None | 5,46 |
| Dzhorsk Formation | 524 | 26,64 | 0,75 | 9,25 | 26,14 | 0,71 | 3,49 | 5,63 | 25,75 | 0,28 | 0,37 |
| | 536 | 19,47 | None | 3,66 | 40,95 | 0,68 | 6,46 | 4,67 | 31,90 | 0,27 | 5,33 |

*MNO — insoluble mineral residue.

The coarse-grained deposits of the Khumarinsk Formation differ in source areas. Conglomerates, gritstones, and sandstones formed as talus-proluvial deposits and the overlying unit of sandstones, as alluvial sediments. The haphazard element distribution in samples from the conglomerates (Fig. 1) was due to their poor sorting. Fe, Ti, Ni, Co, and Cu, sometimes with higher concentrations, occur in Ti-magnetite, magnetite, sphene, and other minerals, preferentially distributed in the rock and occasionally forming local concentrations. It is expected that these ore components occur in higher concentrations because the source area of the rocks was the pre-Jurassic basement that contains polymetallic ore deposits and ore minerals.

The alluvial feldspar—quartz sandstones of the Khumarinsk Formation are much better sorted. The element source of the fluvial deposits are feldspars and the relatively few accessory minerals. Even enrichment of the rock by these minerals resulted in the uniform element distribution pattern in the sandstones. This is indicative of similar formation conditions throughout the unit. Dominance of quartz matter in the alluvial sediments led to the generally lower level of element concentrations.

The characteristic distribution pattern of elements in the Khumarinsk Formation is the result of essentially two factors: (1) the unit is composed products of different degrees alteration; mostly locally eroded rocks of the pre-Jurassic basement with increased concentrations of many elements; (2) the sediments, primarily clayey deposits, accumulated under specific conditions and were significantly enriched in organic plant matter. They were diagenetically strongly reformed and, as the result, the primary geochemical aspects of the sediments were greatly altered.

In the Dzhigiatsk Formation, transition to marine deposits was accompanied by an orderly element distribution in the unit. However, in the Lower Gizhgitsk beds this pattern is complicated by the fact that the Fe and Mn concentration in the clay rocks is somewhat lower (2.68%, respectively, 0.02%; Tables 1 and 2) and in comparison with the "local clarke" values. At the same time, the element concentrations in certain sandstones increased, accompanied by increased carbonate content in the rocks. Such pattern resulted from postdepositional redistribution of the matter in the sediments. As earlier noted, argillites in this unit typically contain abundant siderite concretions and large concentrations of them are common. Although presently organic C is scarce in the clayey rocks, judging from the amount of authigenic siderite, it might be assumed that originally the sediments contained more organic C. This is shown in particular, by the abundance of fine plant detritus. During diagenetic alteration of the sediment, Fe, Mn, and P were involved, possibly with certain trace elements. Redistribution not only concentrated siderite in the concretions, but also resulted in active migration of Fe and Mn bicarbonates in the sandstones and siltstone beds. Local zones of carbonate-cementation developed, often as nodules, in precontact with clay zones, or (when the beds where thin) totally carbonized. The fact that bicarbonate migration from clay deposits into sandy deposits started already during early diagenesis is shown by the siderite concretions that formed in the sands. Later on, the original nodule composition had changed as the result of the erosion of still unconsolidated sediments. In addition, one should consider the possibility that, during later lithogenic stages, the sandstones became carbonized. Kholodov

[20] has shown that this process was widespread during katagenesis in sandy–clayey beds as the result of the hydrolysis of carbonates that are dispersed in the clays. It is difficult to determine the stage in which the postdepositional carbonatization of the coarse-grained rock has taken place. It should be considered as a summary effect of diagenetic and katagenetic migration of matter from compacting clays into the sandstones.

Galena and sphalerite crystals are common in the siderite concretions of the Lower Gizhgitsk beds, indicating Pb and Zn mobility during diagenesis. However, their insignificant redistribution process did not influence the background values of the elements in the rock.

Increased concentration of Zr in the Dzhigiatsk sandstones ($432\text{-}463 \cdot 10^{-4}\%$; Table 3) is essentially the result of zircon content. The mineral is one of the most important component of the heavy mineral fraction [3]. Because zircon is a stable mineral, it may concentrate in nearshore sands and even form placer deposits. Increased Zr content in the sandstones confirms the principle that zircon accumulates in coarse-silty and fine sandy rocks. This pattern was also noted in other north Caucasian stratigraphic intervals [21].

Accumulation of Dzhigiatsk Formation deposits under high wave energy conditions also led to erosional events. Occasional current activity eroded already accumulated sediments and during late Toarcian times iron hydroxide matter was transported from weathering horizons that started to erode from the serpentine-bearing Malkinsk Massif. As the result, the clay–carbonate cement in the concretion conglomerates is enriched in iron. Iron entered the oolites or remained an amorphous iron hydroxide mass.*

The geochemical conditions of deposition during the Aalenian were largely determined by the large quantities of iron that entered the deposits. This caused accumulation of iron and a number of other elements. Introduction of iron matter occurred unevenly; periods of active iron transport, with formation of iron ore beds, alternated with times of clay sediment accumulation. These contained only insignificant or background values of Fe (Figs. 1 and 2). Iron thus was introduced in a pulsating fashion.

Timofeeva [17] studied Aalenian deposits in an adjacent area, NW of the Tyzyl River and, following Efremov [8], believed that iron entered the waters from eroding weathering horizons of the Malkinsk and other massifs. Not all workers shared this view, however [1]. We have also considered the Malkinsk Massif as the most likely source of Fe. Without doubt, during Aalenian the weathering horizon was removed by the northward transgression sea.

The hydroxide paragenesis of iron minerals (hydrogoethite–goethite–hematite sequence), as correctly noted by Timofeeva [17], is a secondary one. Initially, oolites were of chamositic composition. Upward in the sequence the iron ore beds displayed brecciated structures, irregular oolite distribution that included reworked concretions, indicative of sediment accumulation under higher wave energy conditions, accompanied by reworking. It appears that oolite formation did not occur at the burial sites but in areas, closer to the iron source. Currents, primarily short-lived ones, subsequently transported oolites and erosion products, redepositing them. During reworking oolite aggregates formed, coated by a common enveloping layer. At the same time, minerals that formed in reducing media became oxidized. Oolite reworking is indicated also by their fragments; this detritus often occurs in the argillites. Only in certain laters are well-reserved chamositic oolites present that formed in situ. The fact both goethitic and chamositic oolites do occur in the section, the chamositic ones, well preserved, indicates hydroxide mineral paragenesis during sediment accumulation. Retrograde diagenetic processes played but a minor role.

Certain amount of organic carbon apparently became adsorbed on the oolites during their transport. This initiated diagenetic processes in the iron ore beds. In iron-rich sediments, pyrite formed, replacing individual oolites or forming separate precipitates. The solution of numerous carbonate shell fragments and the presence of $Fe^{2+}$ in the sediments led to development of a siderite–calcite cement.

P also entered the deposits with buried organic matter, abundant organic detritus, but evidently primarily in sorbed state in iron hydroxide compounds. In the iron ore layers, especially in the carbonate cement, its concentration was five-times that of clayey rocks.

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*Part of the Fe hydroxides may have formed due to oxidation of the siderite nodules that were eroded out of the sediment and never became hardened.

Iron-rich inner shelf deposits off eastern Australia (Marshall [24]) provide an analog for the Aalenian iron deposits. Marshall noted also Mn- and P-enrichment in the iron deposits. The high P-concentrations are not related to upwelling. The oolites are composed of chamosite and mostly goethite. According to Marshall, as also in our case, goethite formed through chamosite oxidation.

Figures 2 and 3 indicate iron concentration in the ore horizons, accompanied by increased amounts of V and Co. While the V content correlates well with Fe in the similarity in their concentration curves, Co, although it also concentrates in these horizons, does not follow fluctuations of the iron curve as well. The remaining elements in the iron ore horizons show no high concentrations (Ni, Cu) or remain at the same levels as found in argillites (Pb, Ti, and Cr). Ga displayed lesser concentrations than in argillites.

Timofeeva [17] indicated that in the Aalenian section of the Bechasyn Plateau, increasing iron content in the rock is accompanied by increased Ni, Cr, and V content. Co and Cu concentrations remained independent of Fe. Ni and Cr concentrations in the ores are tied to their initial high concentration in weathering horizons of the Malkinsk serpentinites. The low Co content (this element is typical of the Massif) is explainable by its dispersion during sediment transport. Thus, Ni, Cr, and Co tend to concentrate in the Bechasynsk and Tyzyl sections. Certain differences in the geochemical behavior of the iron ore horizons, despite the closeness (30-35 km) of these sections can easily be explained. We believe that this is the result of the complex fate of the iron matter that has undergone various alteration processes between the erosion of the weathering horizon and its final burial. It formed under mildly reducing conditions from iron hydroxides in chamositic oolites, underwent transportation and oxidation, repeated burial, diagenetic alterations, etc.

V in both sections displayed a strong tendency to accumulate with Fe. Our data show that V-enrichment occurs in iron oolite beds at many locations, including Dagestan sections. As is known, iron hydroxides actively adsorb V from sea water [19] — the main reason for the V-enrichment of the iron ore horizons.

In contrast with the enclosing argillites, the oolitic beds contain 1.5-2 times more Ce (40-60, respectively, $90\text{-}120\cdot10^{-4}\%$) than found in analogous horizons in other central Caucasian regions [18]. As Ce accumulates only in these beds in the section, its presence in the sediments must also be associated with iron hydroxide compounds.

Clay beds that include oolite layers, except for higher Fe values (5.59; Table 1), contain elements in concentrations, comparable with values in marine argillites in the rest of the section. In the clay deposits, active concretion development took place during diagenesis. As the result, numerous nodules of mixed siderite—calcite composition and higher P content (Table 4) formed. P entered sediments along with the organic matter and additional iron. Its initial composition apparently was higher than the clarke value.

Recent sediment studies have indicated that P-desorbtion occurs when oxidizing conditions become reducing. Disintegration of organic matter also increases P-enrichment in muddy waters [2]. Similar conditions apparently existed also in the Aalenian sediments: during early diagenesis P and carbonates entered concretions. In contrast with the enclosing argillites, the P-content is several multiples of ten higher in the concretions. In the Aalenian argillites of the Bechasyn Plateau, the iron content is higher, and correspondingly, in sediments with initial high P-content the concretions were even more enriched in P (maximum 14%). Nodules that formed in sediments of the Aalenian basin occur in Lower and Middle Jurassic intervals of higher lime-content (Table 4). The carbonate content was low in the Baksansk argillite beds, as in the other stratigraphic intervals. However, originally the sediments apparently contained large volumes of dispersed biogenic carbonate. During diagenesis, it was dissolved and entered concretions. During the Bajocian transgression, the shoreline moved far north and the Dzhorsk Formation deposits accumulated under deeper marine conditions. An even and relatively low-energy accumulation of clayey and silty—clayey sediments was only rarely interrupted by deposition of fine-sandy deposits in individual beds and members. Such depositional conditions also meant the even distribution of all of the studied chemical elements.

In relatively deep shelf areas reworking of the sediments by burrowing organisms and wave action was of minor extent and organic carbon was oxidized to a lesser degree than in clays of the Dzhigiatsk Formation. As the result, the Bajocian deposits contain more organic C than the Toarcian-Aalenian. This is probably also related to the minor increase in the Mo-content.

In muds of the Bajocian basin, diagenetic processes were less intensive. During early diagenetic stages pyrite formed, later siderite (Table 4, samples 524, 536). In the partially compressed sediments, large limey lenses formed later; some of them with cone-in-cone structure. These included other authigenic new substances. As in the Lower Gizhgitsk beds, migration of Ca, Fe, and Mn-bicarbonates from clays into thick sandstone layers bed to calcite-siderite cement formation in the sandstones. At the same time, the sandstones became enriched in Mo that formed isomorphous admixtures in the carbonates. The rest of the elements are evenly distributed in argillites and sandstones.

Formation of the Bajocian continental, locally coal-bearing Sarydyuz Formation concluded Middle Jurassic deposition. These sediments are enriched in organic plant matter, capable of active chemical reactions. Intensive diagenetic processes occurred. In the aleurolites and sandstones many siderite nodules formed, rendering the beds banded. Lenticular coaly matter formed Fe, Pb, and Zn sulfides in the siltstones. They concentrated as local nodules in thin (0.1 m) sandstone layers that resemble sulfide-bearing sandy layers in coal-bearing argillites of the Khumarinsk Formation. Diagenetic redistribution of the matter and, in particular, participation of Fe, Ca, Mn, Pb, and Zn in the process to a large extent determined the present-day geochemical aspects of these deposits.

* * *

Two intervals occur in the Lower and Middle Jurassic deposits that stand out from the rest: argillites of the Khumarinsk Formation and part of the Baksansk beds with iron oolite horizons. In both instances, a number of elements occur in the rocks with strongly contrasting clarke values. The facies conditions during formation of the geochemical aspects of these sediments played different roles. As shown earlier, the Khumarinsk argillites formed under unusual sediment accumulation conditions, under the influence intensive postdepositional alteration processes. The facies conditions were the determining factors in the composition of lithologic-geochemical aspects of these sediments.

During the Aalenian, throughout the period of Baksansk bed deposition, similar conditions of deposition existed, but with certain individual characteristics. However, in certain stages the uniformity of clay sedimentation were suddently interrupted by a relatively quick impulse of a brief interlude; introduction of iron from eroding weathering horizons. The geochemical aspects of iron ore horizons were inherited from the weathering horizons and acquired during transport into the depositional water basin (V and P accumulation through sorption, and partial loss of Ni and Cr). The two-stage character of element distribution was shown by the diagenetic processes. During diagenesis did accumulation of these muds continue that preceded the "iron ore stage." As noted earlier, in this case, facies conditions in the area of sediment accumulation played a minor role in defining geochemical aspects of the beds.

Comparison of clay deposits in the sequence indicates that uniform element distribution in marine argillites of the Dzhigiatsk and Dzhorsk Formations change in the Khumarinsk Formation to lower concentrations of Fe, Mn, P (down to their disappearance), Ni, Co, Zn, Cu, Ca, Na, carbonate $CO_2$; and to higher concentrations of organic C, Ti, V, Ge, Ga, Mo, Zr, Rb, and Nb. Such geochemical characteristics in argillites, on one hand, indicates regional sediment accumulation characteristics; on the other, reflect the general element distribution features in homogeneous rocks. Tourtelot presented interesting data [27] on element distribution in shallow marine and nonmarine deposits in the interior of North America. His set of data was somewhat different from ours. His continental argillites were subdivided into C-free (inorganic $C < 1\%$; average: 0.2%) and C-bearing (organic C: maximum 17%; average: 2.13%), marine argillites in nearshore ($C_{org} = 0.6\%$) and open marine ($C_{org} = 1.4\%$) settings. His data showed that in comparison with all other sediments, in coal-bearing continental argillites Ni, Co, Zn, Cu, V, and Cr are of lower concentration, while the Zr-concentration increased greatly and the Pb-values of increase were insignificant. As noted, the behavior of Ni, Co, Zn, Cu, and Zr was similar to that observed by us, and, in all likelihood resulted from similarities in characteristics of sediment and rock formation in continental deposits that contain large amounts of organic plant matter.

Certain similar features were also observable in element distribution in Namurian marine and continental black shales of England, studied by Spears and Amin [25]. In marine shales, Ni, Zn, Cu, Pb, and V had high concentrations, while in the continental shales: Zr and Mn. The Mn values were due to presence in siderite. Co, Cr, Rb, and Y had relatively uniform concentrations. Zr displayed a consistent association with continental black argillites.

Kholodov and Nedumov [22] studied in detail the geochemistry of Middle Miocene deposits of the eastern Precaucasus, deposited in a water basin of an intermontane depression. However, the element distribution in clay rocks of this sequence and marine argillites of the Tyzyl section very similar. Only the Middle Miocene deposits display black clay horizons, greatly enriched in organic matter, comparable in organic carbon content with Pliensbachian argillites. Nevertheless, the composition of the black clay resembles that of the Jurassic marine argillites. Thus, even when the quantitative (but not qualitative), parameters in the organic matter were similar to those in sediments that formed under sharply differing facies conditions, there were much fewer common traits than found in marine deposits. This happened despite the essentially different amounts of organic carbon.

The low concentrations of a number of elements (Fe, Mn, etc.) in lacustrine-swamp deposits are due primarily to redistribution and removal of these elements from the sediments in an acid medium, through extraction even from silicates and other minerals. In marine deposits in which, as in present deposits, the pH value sharply drops below 7, such active disintegration of terrigenous minerals did not take place. During diagenetic redistribution, those elements were primarily involved that are adsorbed on clay particle and organic matter surfaces. They participated in the hydroxide compounds of the sediments. Sulfate-reduction in marine muds resulted in sulfides of low mobility. These incorporated a number of elements into the sediments.

The various sediment formation conditions resulted in the uneven distribution of certain minerals in the layers. Thus, continental argillites display an essentially kaolinitic composition, noted by several workers in other regions [23, 25, etc.]. While sulfide mineral lenses and nests in the Khumarinsk deposits occur only in coal-bearing layers and in sand layers in their immediate vicinity, in the Dzhigiatsk and Dzhorsk rocks small sulfide clusters and nodules (essentially pyrite) are very widespread. Siderite forms as a "polyfacies" mineral, in practically all types of deposits.

The element distribution pattern in sandy, as well as in clay rocks is uneven in the sequence. Coarse-grained rocks of the Khumarinsk Formation show uneven element distribution; in certain samples their concentration is higher than in clayey rocks, in others, lower. This is quite typical of poorly sorted continental deposits [15]. In the Dzhigiatsk and Dzhorsk Formation an even element distribution pattern is most characteristic. However, this pattern occasionally changes, due to two factors. First, postdepositional migration of Fe, Mn, Ca-bicarbonates and P from clays into sandstones increased concentrations of these elements. Second, the widespread distribution of zircon in the fine-grained Dzhigiatsk sandstones more than doubled the Zr content, in comparison with argillites. The sandstones also concentrated Cr; its value was the same or even higher than in the argillites.

The relatively thin $J_{1-2}$ section and the enclosed sediments that accumulated in various continental and marine shelf facies with their own particular geochemical characteristics, differ markedly from the Lower–Middle Jurassic Labin-Malkinsk section in the central Caucasus. The sand–clayey beds of that zone, further to the south, on the northern margin of the Jurassic geosyncline, are thick, and monotonous in composition.

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