Lithology and Mineral Resources, Vol. 39, No. 2, 2004, pp. 156–168. Translated from Litologiya i Poleznye Iskopaemye, No. 2, 2004, pp. 185–199.
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Clay Mineral Associations in Triassic–Lower Cretaceous Rocks of the Dal'negorsk Key Section, Southern Sikhote Alin

M. I. Tuchkova[1], N. Yu. Bragin[1], and K. A. Krylov[2]

[1] *Geological Institute, Russian Academy of Sciences, Pyzhevskii per. 7, Moscow, 119017 Russia*
e-mail: tuchkova@ginras.ru
[2] *Stanford University, Stanford, USA*

Received June 18, 2003

Abstract—Investigation of the Triassic–Lower Cretaceous rocks of the Dal'negorsk key section (southern Sikhote Alin) revealed the following successive associations of authigenic clay minerals: (1) sericite–chlorite (Lower Triassic); (2) mica–chlorite (Anisian–Norian); (3) chlorite–mica (Rhaetian–Lower Jurassic); and (4) smectite–chlorite–mica (Upper Jurassic–Lower Cretaceous). These four associations reflect the primary composition of terrigenous admixture in the siliceous sediments and, hence, serve as important indicators of paleosedimentation conditions. The first association represents a product of the erosion of metamorphic rock complexes. The second one reflects the onset of volcanic activity within the sedimentation basin coinciding in time with a vigorous bloom of siliceous plankton (radiolarians) and short-term appearance of specific (anoxic) carbonaceous sediments in the sequence. The third association characterizes the epoch of minimal supply of the basin with volcanic and terrigenous clastic materials and the dominant accumulation of almost pure planktonogenic sediments. The fourth association marks the change of marginal-marine conditions for pelagic ones and is expressed in a significant input of pyroclastic and clastic materials and the formation of distal flysch deposits.

Siliceous rocks always contain different clay minerals that are of undoubted interest for the reconstruction of formation conditions of these rocks. However, until recent times, their mineral composition and distribution pattern were not sufficiently studied and could not be adequately used. At present, study of clay minerals with the help of high-precision methods allows us to reveal their structural characteristics and genesis. Therefore, the establishment of clay mineral associations and their distribution pattern in siliceous rocks is a pressing issue. Study of clays in Mesozoic and Paleozoic siliceous rocks of northeastern Russia revealed a primarily allothigenic origin of terrigenous admixture in cherts (Volokhin, 1980; Konstantinovskaya, 1997, 1998; and others). Recent development of the detailed (zonal) stratigraphy of Mesozoic siliceous sequences has created favorable conditions for the precise stratigraphic correlation of the studied mineral associations and the analysis of their changes and evolution in sedimentary sequences in key sections. This paper presents results of the study of clay minerals from the Triassic–Jurassic key section of siliceous members near the Settlement of Dal'negorsk along the Rudnaya River in southern Sikhote Alin. The section is subdivided into zones based on radiolarians. In this section, we previously established the main levels of taxon changes, calculated sedimentation rates, and defined characteristic radiolarian associations for each time interval (Bragin, 2000).

MATERIALS AND METHODS

Clay minerals were studied in several stages. First, clay minerals and (or) their associations were investigated in thin sections. We also carried out the petrographic description of siliceous rocks. The clay component was separated in accordance with the standard procedure: decantation of clay fraction and preparation of oriented specimens. Composition of clay minerals in fraction <0.001 mm was determined by the X-ray diffraction analysis. The most representative samples with the maximum content of clay minerals were analyzed by the microprobe method with the quantitative determination of major oxides. Morphological features of clay minerals were defined using a scanning electron microscope.

The radiolarian shell content was calculated in all samples with a POLAM L-213M microscope based on 5 measurements at each point (magnification 100).

GEOLOGICAL SETTING AND LITHOLOGICAL CHARACTERISTICS OF THE DAL'NEGORSK SECTION

Mesozoic siliceous rocks are widespread in northeastern Russia (Sikhote Alin, Koryakia, Sakhalin, and other regions). These rocks or their fragments are exposed in many terranes of the Pacific Belt. Their structure has been scrutinized in Kamchatka (Grechin, 1972), Primorye (Volokhin *et al.*, 1989, 1990; Volokhin, 1980; Kemkin and Kemkina, 1998; Bragin,

Table 1. Composition of chlorites from siliceous rocks

Components	Siliceous–clayey rock	Siliceous–clayey rock	Siliceous–clayey rock	Siliceous–clayey rock	Clay-poor siliceous rock	Clay-poor siliceous rock
	T_1o_2	T_1o_2	T_3n_{1-2}	T_3n_{1-2}	T_3r	T_3r
	19/30	19/30	19/64	19/64*	19/77	19/77
SiO_2	29.666	29.036	26.160	25.667	25.454	25.291
Al_2O_3	20.294	19.014	20.01	27.871	23.322	23.040
FeO*	28.385	29.273	33.64	31.292	30.649	30.815
MgO	12.080	13.446	8.336	6.595	8.406	8.075
CaO	0.123	0.041	0.089	0.085	0.074	0.052
K_2O	0.064	0.046	0.062	0.699	0.031	0.169
total	90.611	90.856	88.297	88.209	87.936	87.442

Note: Based on electron probe microanalysis (G.V. Karpova, analyst; Geological Institute, Moscow); (*) Chlorite in veinlet; the rest in host rock.

1991, 2000; Bragin *et al.*, 2002), Taigonos Peninsula (Konstantinovskaya, 1998), and the southern Sredinnyi Ridge of Kamchatka (Konstantinovskaya, 1997). In the Primorye accretionary belt, Mesozoic oceanic complexes mainly consist of effusive siliceous, tuffaceous–siliceous, and siliceous–clayey rocks. Siliceous rocks are the principal component of Mesozoic sequences (Volokhin *et al.*, 1990; Bragin, 1991; Golozubov and Mel'nikov, 1986). In Primorye, the structure of terrigenous–siliceous sequences was scrutinized at the Rudnaya River in the Dal'negorsk region ore district, Sikhote Alin (Volokhin *et al.*, 1990; Volokhin, 1980; Kemkin and Kemkina, 1998; Bragin, 1991, 2000; Bragin and Krylov, 2002). The Dal'negorsk ore district is located within the Taukha terrane (Fig. 1), which is an Early Cretaceous accretionary prism (Golozubov *et al.*, 1992; Kemkin and Khanchuk, 1993; Kemkin and Kemkina, 1998). The Taukha terrane is characterized by multiple alternations of turbiditic olistostrome and paleoceanic rocks and the development of complicated nappes with the juxtaposition of heterogeneous tectonic slabs. One of these slabs composed of Triassic–Early Cretaceous siliceous rocks crops out along banks of the Rudnaya River at the eastern periphery of Dal'negorsk (Fig. 1a). The sequence includes different Triassic–Lower Jurassic siliceous, Early Cretaceous flyschlike rocks, and pillow basalts alternating with late Carnian red massive radiolarian cherts in the middle section (Fig. 2).

The Dal'negorsk section is the reference sequence for the Triassic and Jurassic radiolarian zonal stratigraphy in the Far East (Bragin, 1991, 2000; Kemkin and Kemkina, 1998). However, some points in the available stratigraphic scale for this region still remain debatable. Dating of the lower part of the section meets some difficulties and is least substantiated because of the scarcity or even absence of radiolarians in the Early Triassic (Bragin, 2000). Induan rocks are only provisionally dated. Any definable fossils have not been found in them, and their stratigraphic allocation is based on the position in the sequence below the dated Olenekian and the lithological similarity with Induan rocks in Japan (Ishiga *et al.*, 1996; Kukuwa, 1996; Yamakita *et al.*, 1999). The supposed Induan sequence mainly consists of coaly shales (up to 8 m) represented by clay-poor silicite with abundant dispersed organic material and rare silt particles. Indefinable, partially sulfidized plant remnants are also abundant. Iron hydroxides are developed in caverns, veinlets, and fractures. Clay minerals make up tiny (0.01–0.02 mm or less) aggregates (Fig. 3a). Based on X-ray spectroscopy, the clay mineral association of this age interval includes micaceous mineral of the sericite type with a small admixture of chlorite.

Lower Olenekian members are composed of cherts with sponge spicules. Radiolarians are rare in this part of the section, and the dating is based on typical conodonts. Thin interlayers of silica-rich spongolites composed of redeposited fragments of large spicules (macroscleres) are common in the sequence. The Toishi shale in Japan (Matsuoka *et al.*, 1994) is a stratigraphic and lithologic analogue of these rocks. In contrast, upper Olenekian cherts consist of radiolarians, and sponge spicules are rare. The section includes radiolarite interlayers with occasional sorting of radiolarian remnants and red-colored cherts enriched in iron hydroxides.

Microscopic study showed that the Olenekian rocks consist of a silty–siliceous substance with rare individual silica pseudomorphs after deformed radiolarian shells and finely and uniformly dispersed organic material. The siliceous matrix includes fine sericite flakes, 0.01–0.02 mm or less in size, locally characterized by unidirectional orientation. In veinlets and some interstices, the sericite is associated with iron hydroxides, ferruginous chlorite flakes (0.01–0.02 mm in size), authigenic quartz, and carbonate (Table 1). In some interstices, only relict chlorite is noted, because it is almost completely replaced by carbonate. The clay

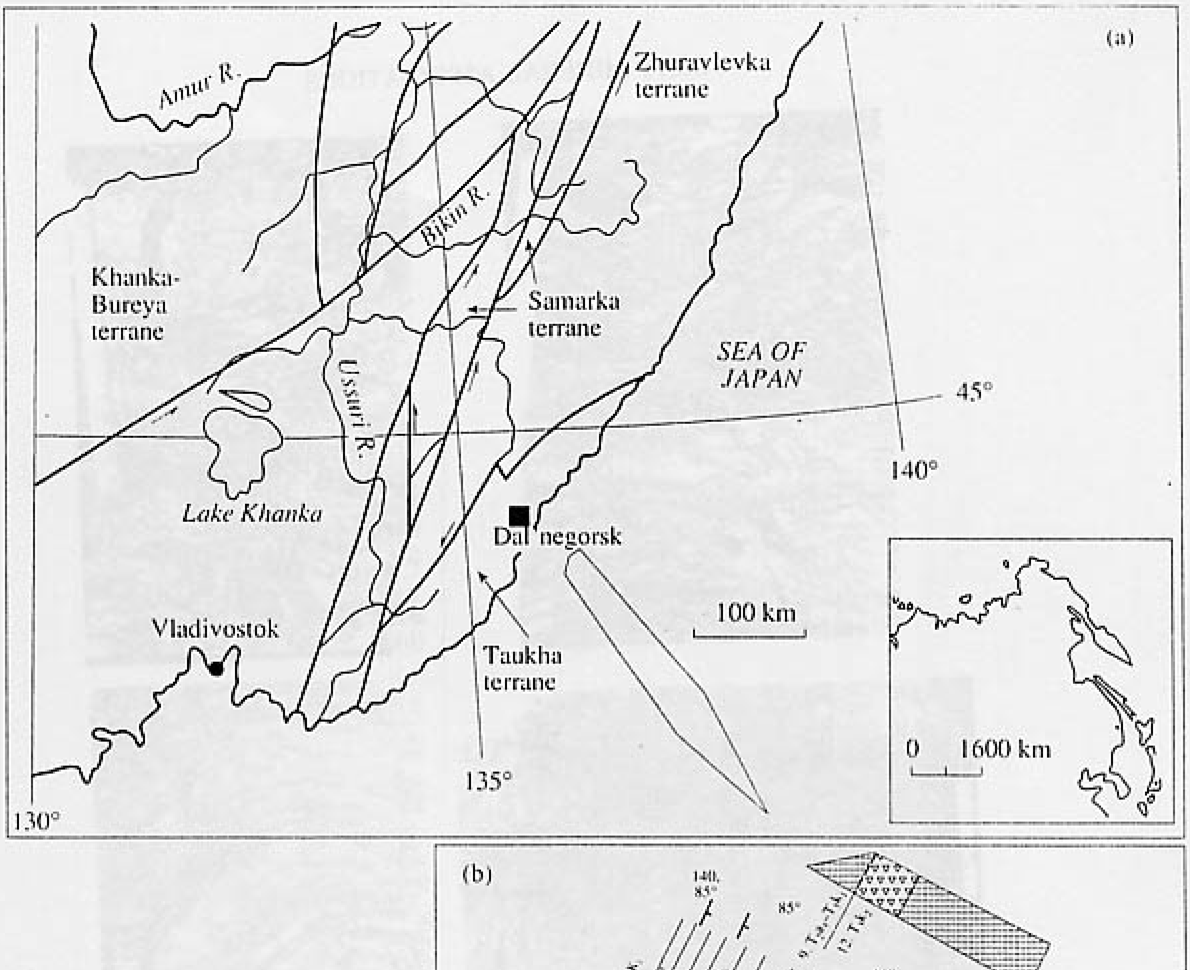

Fig. 1. Geotectonic structure of the southern Sikhote Alin region. (a) Tectonic scheme (after Natal'in, 1991). Inset shows location of the region. (b) Geological scheme of the key section of Triassic rocks along the Rudnaya River near Dal'negorsk. (1) Lower Cretaceous terrigenous rocks (predominantly sandstones); (2) siliceous mudstones and mudstones with spongiolite chert interlayers; (3) gray radiolarian cherts; (4) basic lavas; (5) alternation of biogenic cherts, tuffosilicites and siliceous mudstones; (6) mudstones with thin oblique-bedded sandstone interlayers; (7) alternation of sandstones, siltstones, and mudstones; (8) carbonaceous mudstones and phtanites; (9) faults; (10) dikes of intermediate composition; (11) age allocation; (12) rock occurrence mode.

matrix content is low. Therefore, the clay fraction content is also low. Based on X-ray spectroscopy, clay minerals are represented by sericite with a minor admixture of chlorite.

The number of radiolarite interlayers increases and carbonaceous rock horizons appear in lower Anisian sequences (Bragin and Krylov, 2002). The carbonaceous rocks make up thin beds in a monotonous intercalation of siliceous mudstones and radiolarian cherts. The carbonaceous horizons have sharp and distinct contacts with enclosing rocks. They are characterized by enrichment in organic material and sulfides (pre-

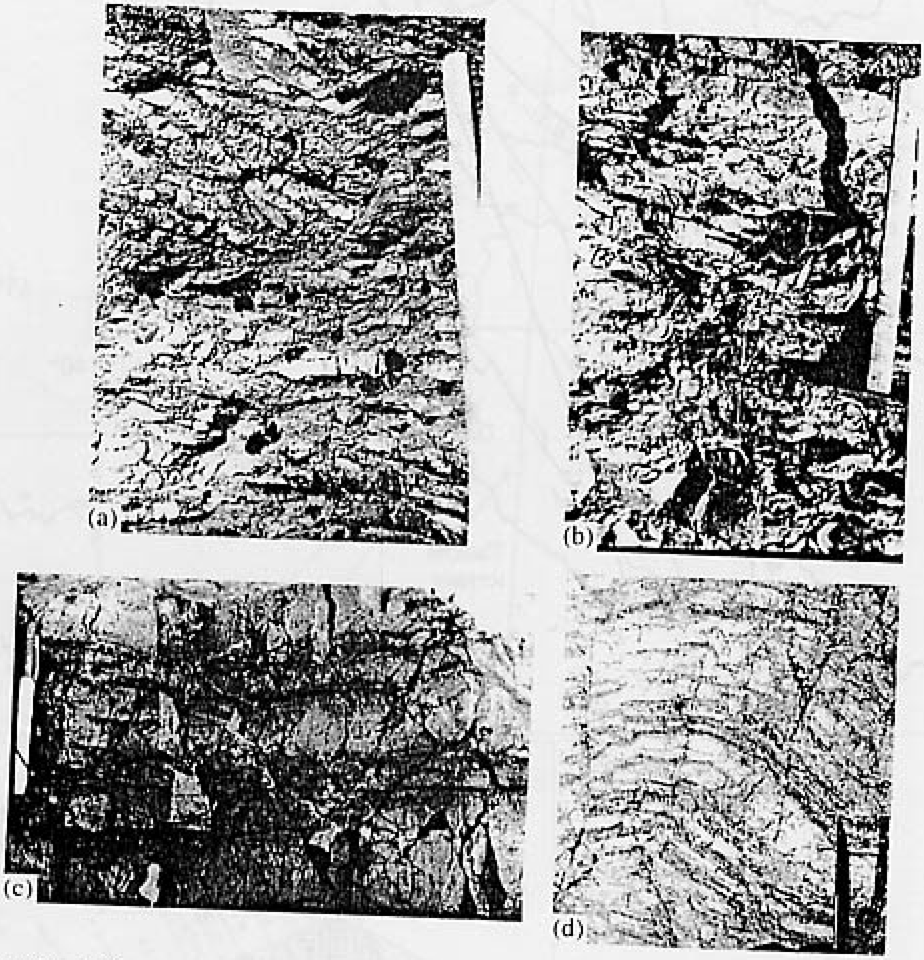

Fig. 2. Type photographs of siliceous rocks from the Rudnaya River. (a) Olenekian rocks of the Lower Triassic (T_1o_2), (b) Anisian rocks of the Middle Triassic (T_2a_2), (c) lower–middle Norian rocks of the Upper Triassic (T_3n_{1-2}), (d) Rhaetian rocks of the Upper Triassic (T_3r).

dominantly, pyrite). The lower Anisian rocks are clayey radiolarites with strongly deformed radiolarian remnants. Primary sedimentary structures are absent. Middle–upper Anisian rocks are noted by the predominance of radiolarites over siliceous mudstones. The sequence is characterized by alternations of interlayers with a variable content of radiolarian remnants. The thickness of the Anisian sequence is approximately 25 m.

The microscopic study showed that the Anisian clay-poor silicites consist of fine-grained cryptocrystalline quartz aggregates and almost undistinguishable individual aggregates. Radiolarian remnants are composed of cryptocrystalline quartz with an admixture of dispersed hematite (Fig. 3b). The interstitial matrix with radiolarian remnants is composed of fine-dispersed siliceous substance containing a small amount of plant remnants, sulfide minerals, and zeolites (not more than 3–5%). The content of clayey constituents irregularly changes through the section. Their aggregates are up to 0.01 mm in size. Sericite and chlorite are the major clay minerals. The chlorite content gradually increases upward the Anisian sequence. Sometimes micaceous mineral aggregates form clusters and patches with distinct sericite flakes characterized by reduced interferential color. The rock is generally crosscut by different-sized veinlets with spherical aggregates of ore mineral. The veinlets are filled with iron hydroxides and chlorite and micaceous mineral flakes. Quartz aggregates (or siliceous substance similar to the host rock) is developed in the central part of relatively large veinlets.

The overlying late Anisian–early Carnian sequence (~35 m thick) includes pale gray cherts and red-brown jaspers. The rocks contain almost undeformed remnants of radiolarians, their spines, and other organic remnants. The low-clay silicites consist of cryptocrystalline quartz with practically undistinguishable aggregates and disseminated ore minerals. The rock is usually crosscut by numerous chaotically oriented veinlets with chalcedony in peripheral parts. The central zone of veinlets consists of fine scaly aggregates of brownish green chlorite occasionally associated with sericite and iron hydroxides. The clay mineral aggregates do not exceed 0.01 mm in size.

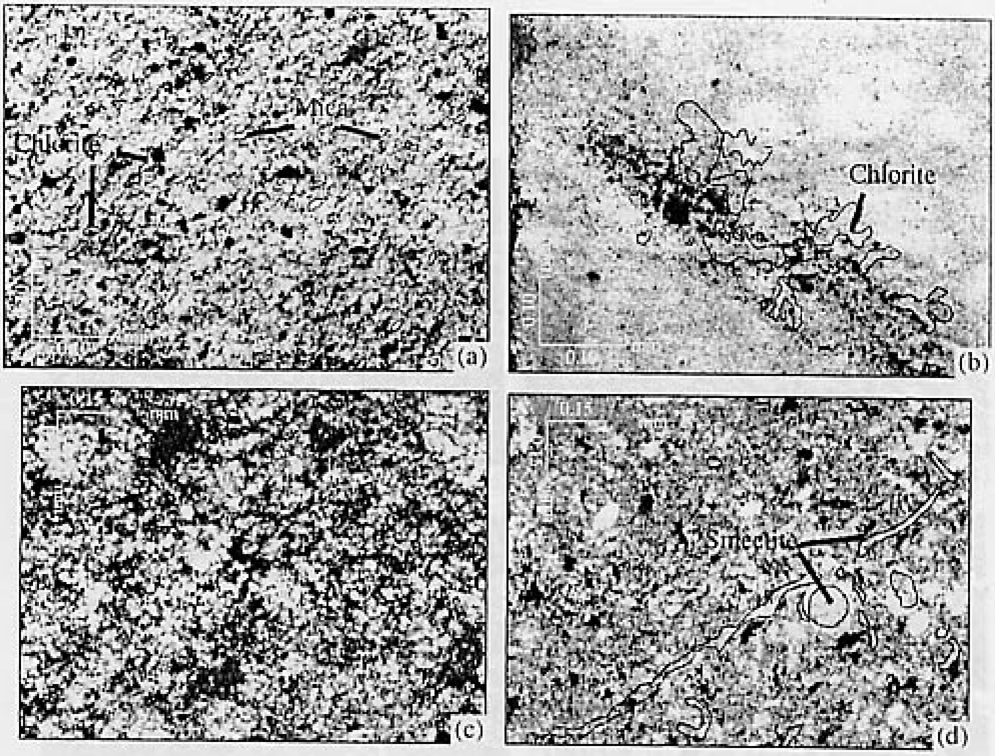

Fig. 3. Type thin sections of cherts from different parts of the Rudnaya River section. (a) Siliceous mudstone with partly sulfidized plant remnants (black) and poorly distinguishable flakes and aggregates of sericite. Induan(?). Sample 19-2. (b) Siliceous rock consisting of cryptocrystalline quartz and some radiolarian relicts. Clay material (chlorite and mica) is present in the form of separate flakes or aggregates. Middle Anisian. Sample 19-54. (c) Silicite with a high content of radiolarian remnants and some sulfidized organic material (black). Clay minerals are almost absent. Radiolarian shells are filled with chalcedony (in central parts) and cryptocrystalline quartz (in peripheral parts). Lower–Middle Jurassic (J_1p_2-J_{2a}). Sample 19-80. (d) Siltstone–mudstone with a high content of clay minerals and dispersed organic material. Radiolarian shells consist of smectite (in central parts) and cryptocrystalline quartz (in peripheral parts). Upper Jurassic–Lower Cretaceous (J_3t-K_1v). Sample 19-100.

The overlying upper Carnian basalts contain thin interlayers and rare lenses (0.5–2 m) of red-brown jaspers with radiolarians, foraminifers, and conodonts.

The Norian sequence, about 20 m thick, includes gray cherts of different tints with rare interlayers of yellowish gray siliceous mudstones. Microscopic study showed that they are made up of cryptocrystalline quartz aggregates with vague grain boundaries and fine-dispersed ore material. Rare relicts of undeformed radiolarians and their spines are composed by cryptocrystalline siliceous material or chalcedony. One can note a zonation in the radiolarian composition: the central part of their shells is composed of chalcedony, whereas the periphery includes small aggregates of cryptocrystalline quartz. The number of radiolarians with chalcedony infilling significantly increases in Upper Triassic rocks in comparison to Middle Triassic rocks. Sectors between radiolarians contain a large amount of fine, differently oriented flakes of chlorite and micaceous mineral. In some cases, mica aggregates with subdued interference color form clusters. Chlorite is observed as flaky and less common rosette-shaped pale green individuals. Both Norian and more ancient rocks are characterized by the abundance of differently sized and oriented veinlets filled with fine-grained quartz aggregates, fine-scaly chlorite aggregates, rare flakes of micaceous mineral, iron hydroxides confined to peripheral areas of the veinlets, and minor zeolite usually developed in veinlets with quartz infilling.

Rhaetian silicites, more than 8 m thick, are composed of gray, dark gray, and greenish gray fine-platy cherts with interlayers of light gray massive silicified cherts and rare interlayers of brownish gray siliceous mudstones. The silicites consist of fine-grained cryptocrystalline quartz, fine-dispersed ore and organic materials, and an insignificant amount of undeformed radiolarians with chalcedony infilling and vague boundaries. The content of clay minerals is low. They are observed as pale green fine-scaly chlorite and minor micaceous mineral.

Bright olive-green chlorite often associated with iron hydroxides and some quantity of micaceous and ore minerals is developed in thin veinlets (1–1.5 mm). In some places, the rock contains abundant veinlets, which often intersect each other and make up isolated sectors (pseudoglobules) filled with siliceous material or chalcedony.

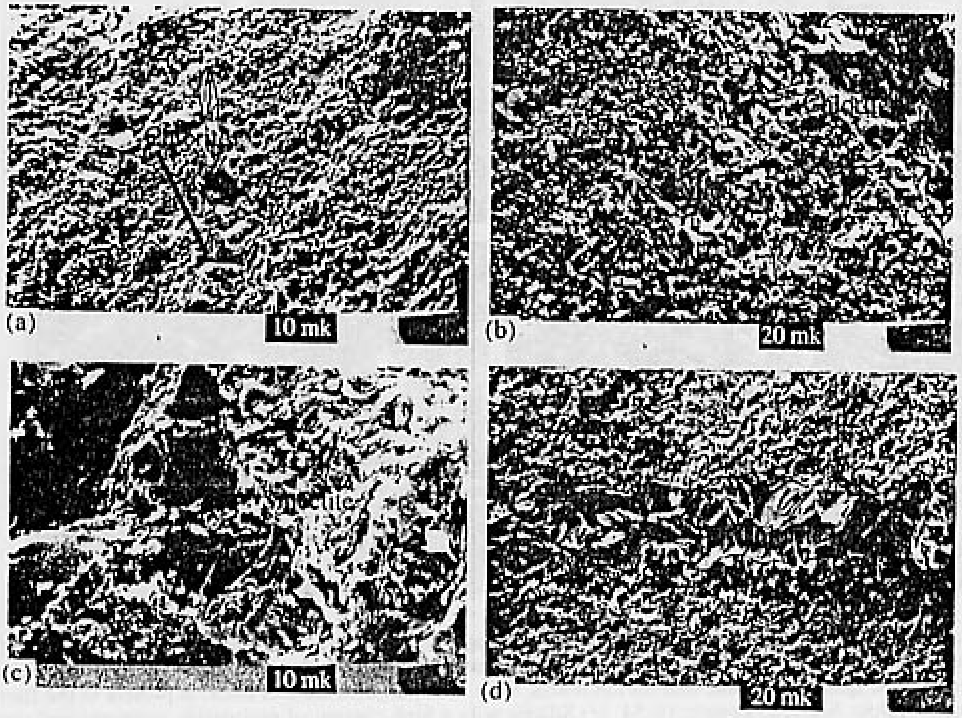

Fig. 4. Type photographs of clay minerals (SEM images). (a) Mica flakes in quartz matrix. Induan (?). Sample 19-11. (b) Mica flakes in the siliceous matrix. Norian Stage of the Late Triassic. Sample 19-70. (c) Smectite flakes developed on volcanic glass fragment. Lower Cretaceous. Sample 19-100. (d) Chlorite flakes filling fracture in rock. Induan (?). Sample 19-11.

Jurassic siliceous rocks in the section are represented by bright gray cherts and occasional jaspers. The Early Jurassic silicites consist of fine-grained quartz with mosaic extinction. The rock contains fine-dispersed clayey material and large iron hydroxide segregations (Fig. 3c). The content of radiolarian relicts is high. Their shells are undeformed and filled with chalcedony in the central part and cryptocrystalline quartz at the periphery. The content of clay minerals in Early Jurassic cherts is n%. The rock contains rare, very fine flakes of chlorite and micaceous mineral (not more than 0.5 vol % in thin sections). Authigenic quartz, flakes of brown-green chlorite, and micaceous mineral develop in numerous differently oriented veinlets. In some places, the veinlets contain only iron hydroxides (probably, hematite).

Upper Jurassic–Lower Cretaceous rocks are composed of flyschlike alternation of fine-grained polymictic sandstones and mudstones. The clastic fraction includes plant remnants, radiolarians, fragments of siliceous rocks and quartz, and clay minerals. Interstices are practically absent. Clasts and organic remnants are contained in a hydromicaceous fine-dispersed matrix probably consisting of a mixture of clay minerals, fine-dispersed organic and ore materials, and fine-grained terrigenous component (Fig. 3d). The content of clay minerals in the rock is high. They include mica, smectite (Fig. 4), and minor chlorite. Radiolarian shells are weakly deformed. Their central parts are composed of clay mineral (probably, smectite), whereas the peripheral parts consist of cryptocrystalline quartz.

Thus, Triassic–Jurassic siliceous rocks are subsided into the following four associations of authigenic clay minerals grading into each other with time (Fig. 5): (1) sericite association with minor chlorite (Induan–upper Olenekian); (2) mica–chlorite association with a gradual decrease of the mica content and increase of the chlorite content upward the sequence (lower Anisian–Norian); (3) chlorite–mica association with a low content of clayey material (Rhaetian–Lower Jurassic); and (4) smectite–chlorite–mica association (Upper Jurassic–Valanginian).

Moreover, relicts of Olenekian–middle Anisian radiolarian shells filled with siliceous mass are replaced upsection by Carnian–Rhaetian radiolarians filled with chalcedony. The content of shells filled with chalcedony is low (3–5%) in the pre-Carnian, increases in the middle Carnian (15–20%), and reaches the maximum (80%) in the post-Carnian time. In jaspers associated with upper Carnian basalts, radiolarian relicts are filled with cryptocrystalline quartz (peripheral zone) and smectite (central zone) rather than chalcedony.

LITHOLOGICAL–MINERALOGICAL, GEOCHEMICAL, AND FAUNAL FEATURES OF THE SILICEOUS ROCKS

Starting with the Anisian layers, radiolarian remnants are apparently a constant component of sedimen-

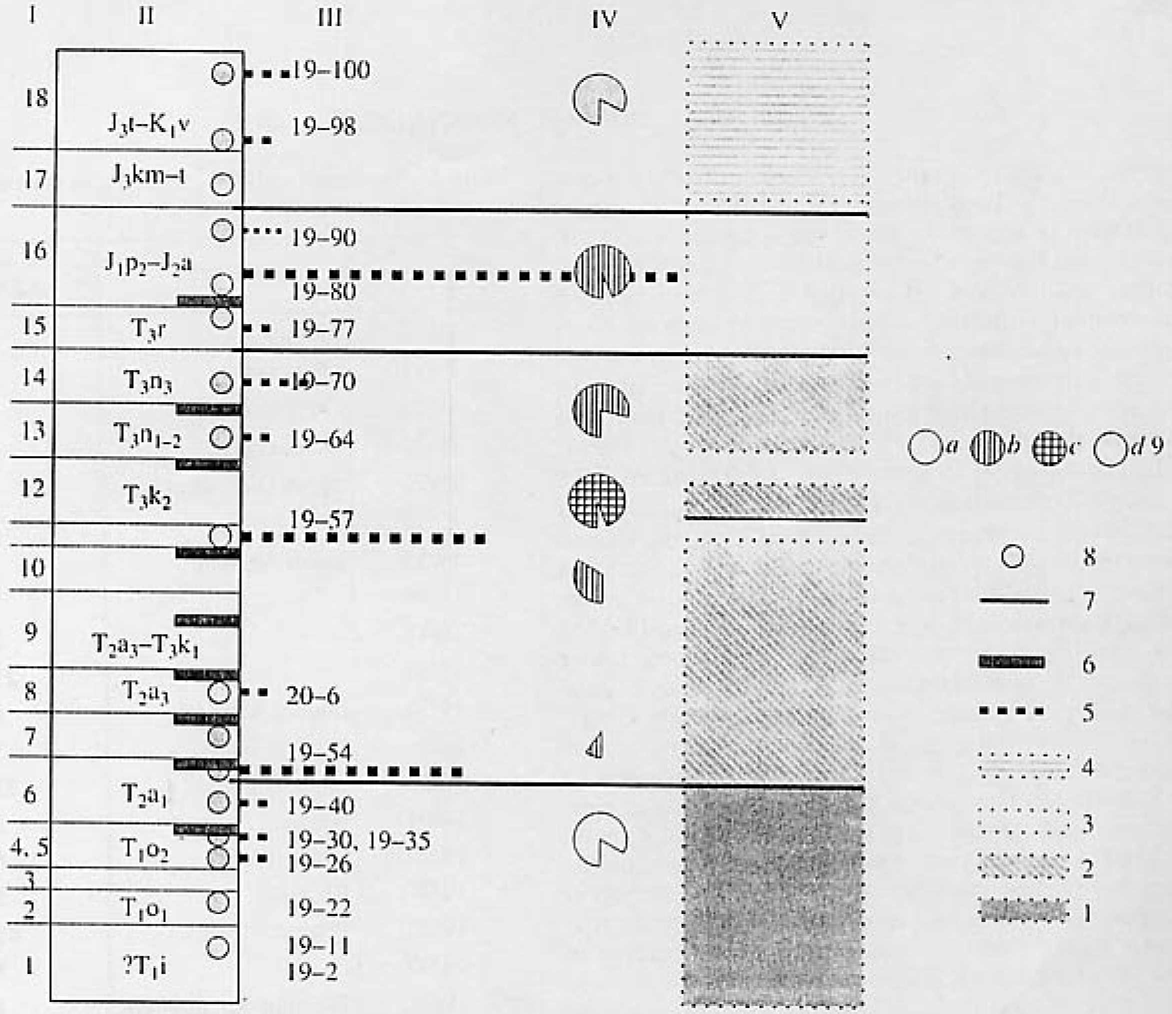

Fig. 5. Distribution and composition of clay minerals in the Rudnaya River section. (I) Layer numbers in the sequence (correspond to numbers in Fig. 1b), (II) section with indicated age of layers, (III) sample numbers, (IV) infilling of radiolarians with quartz (size of fill areas corresponds to the percentage of radiolarians filled with different types of quartz), (V) clay mineral associations: (1) sericite with a minor chlorite admixture (Induan–upper Olenekian); (2) mica–chlorite with gradual upsection decrease of mica and increase of chlorite (lower Anisian–Norian); (3) chlorite–mica, the rock is characterized by low content of clay material (Rhaetian–Lower Jurassic); (4) smectite–chlorite–mica (Upper Jurassic–Valanginian), (5) peaks of radiolarian assemblages, (6) boundaries of changes in radiolarian assemblages, (7) boundaries of changes in clay mineral associations, (8) sample location and number in stratigraphic section; (9) infilling of radiolarians: (*a*) cryptocrystalline quartz; (*b*) chalcedony, (*c*) lutecite, (*d*) smectite.

tary rocks in the Dal'negorsk section. However, the sequence includes rocks characterized by a wide variation of the content of radiolarian skeletons. Locally, the rocks are almost completely composed of the skeletons (radiolarites). The calculation of radiolarian remnants in thin sections made it possible to reveal three peaks related to sharp increase in the concentration of organic remains in the siliceous rocks. The first maximum is observed at the boundary between the early and middle Anisian (Sample 19-50). The second maximum is located in a lenslike jasper interlayer sandwiched between basaltic flows in upper Carnian rocks (Sample 19-57). The third, quantitatively most pronounced maximum shows up in Lower Jurassic rocks (Sample 19-80). The remaining horizons characterized by the disappearance or appearance of new radiolarian assemblages contain a relatively stable amount of organic remnants (Table 2). The lower (Anisian) and upper (Triassic–Jurassic) peaks immediately overlie carbonaceous mudstone units, which indicate the manifestation of anoxic events (Bragin and Krylov, 2002). The middle (upper Carnian) maximum is observed after the appearance of basalts in the sequence. Radiolarites from the anoxic horizons are strongly cleaved. Spheroid radiolarians are flattened and characterized by partially dissolved skeleton.

These peaks testify to blooms of the radiolarian productivity in the marine basin. Since two peaks in the Dal'negorsk section are related to the termination of early Anisian and early Toarcian anoxic events, their relation with the radiolarian bioproductivity is evident. The subsequent blooms of siliceous plankton are proven for many anoxic events in the World Ocean. Thus, the early Toarcian episode in siliceous members in Japan was accompanied by the appearance of radiolarites and the significant qualitative growth of radiolarian assemblages (Hori, 1993). The well known Cenomanian–Turonian anoxic event in carbonate-terrigenous sequences of the Mediterranean and Crimea preceded the appearance of substantially siliceous radiolarites that form the regionally persistent Bonarelli Horizon (Kuhnt *et al.*, 1986; Marcucci *et al.*, 1991; O'Dogherty, 1994; Bragina *et al.*, 1999). Meanwhile, the early Turonian was marked by both quantitative and qualitative enrichment in radiolarians probably due to increase of phytoplankton bioproductivity. Such an intense bloom of bioproductivity in marine basin arises during transgressions when vast lowlands are flooded and lacustrine-swamp landscapes are formed under conditions of humid climate. Based on the study of several geological objects, Gavrilov *et al.* (1996, 1997, 2002) convincingly proved the fact mentioned above. Vigorous development of phytoplankton triggers a short-term acceleration of siliceous zooplankton productivity (radiolarians), on the one hand, and oppression and even extinction of benthonic organisms, on the other hand, when anoxic conditions spread in near-bottom parts of a basin. One more, not less significant reason for biotic events are volcanic processes leading to changes in the chemical composition of sea water and interaction of basaltic lavas with sea water at high temperatures. Researchers have drawn attention to the link between global deep-water anoxic events and outbursts of volcanisms (Bralower *et al.*, 1993; Volokhin *et al.*, 1990; Kaipov and Levin, 1982; Krasnyi and Mikhailov, 1966). Thus, at least two factors (transgressions and outbursts of volcanism) lead to increase in siliceous plankton (radiolarian) productivity.

According to the available interpretations, siliceous sequences of the Russian Far East are planktonogenic sediments of the pelagic zone of a paleocean. The rate of siliceous sedimentation is estimated at 1.6 mm/ka (or 4.8–9.6 mm/ka if the compaction is taken into account) (Bragin, 1991). Study of siliceous rocks in southern Sikhote Alin revealed that cyclicity of siliceous beds is dictated by the periodic impulsive input of terrigenous fine-grained (clay) material during the formation of clay elements of the cyclites against the background of a continuous and slow settling of radiolarian skeletons (Volokhin, 1980, 1985, 1988; Mazarovich, 1981, 1985; Mazarovich and Rikhter, 1985; Konstantinovskaya, 1998). Clay minerals found in the siliceous sequences are allothigenous components; i.e., they were supplied from outside. Their association was governed by the erosion of continental clastic components. Siliceous rocks formed due to both biogenic (radiolarites and spongolites) and terrigenous (clays) sedimentation.

The studied siliceous rocks can be compared with the coeval sandstones accumulated in the same structural zone. In (Volokhin, 1988; Markevich, 1978; Markevich and Konovalov, 2000; and others), sandstones of the Gorbusha and Taukha formations are referred to as arkose-graywackes based on the classification diagram of Shutov (1972). Arkosic and quartzose–sandy materials prevail in Lower Cretaceous rocks. Acid crystalline rocks (similar to granites and metamorphic rocks), as well as sedimentary and intrabasinal basic volcanic rocks, probably served as the provenance for these rocks. Terrigenous admixture in cherts depends on the composition of the provenance, and the change in clay mineral associations indicates the change in the source during sedimentation. However, the vertical succession described above can be related to not only changes in provenances but also to lithogenetic transformations of the siliceous sequence. The X-ray structural analysis (Grechin, 1972; Volokhin, 1989) is one of the important methods for determining the rate of postsedimentary changes in siliceous rocks. The X-ray diffraction analysis makes it possible to define the composition of clay minerals and the forms of silica segregations. The X-ray diffraction patterns indicate that the siliceous rocks are only composed of quartz. Less stable varieties of silica (opal, crystobalite, and others) are absent, suggesting a rather high metamorphism grade of siliceous rocks in the Rudnaya River section.

Parageneses of clay minerals, as well as their chemical and structural features, are also indicators of the

Table 2. Number of radiolarian shell remnants calculated in thin sections

Sample no.	Age	Number of radiolarians
19/–2	Induan(?)	0
19/–10	Olenekian	1
19/11	Olenekian	0
19/22	Olenekian	2
19/26	upper Olenekian	2
19/30		36
19/35	lower Anisian	3
19/40		3
19/47		28
19/50		218
19/54	middle Anisian	17
20/6	upper Anisian	38
19/57	upper Carnian	235
19/64	Norian	29
19/70	upper Norian	65
19/77	Rhaetian	58
19/80	Pliensbachian	490
19/90		58
19/98	Titonian–Valanginian	18
19/100		4

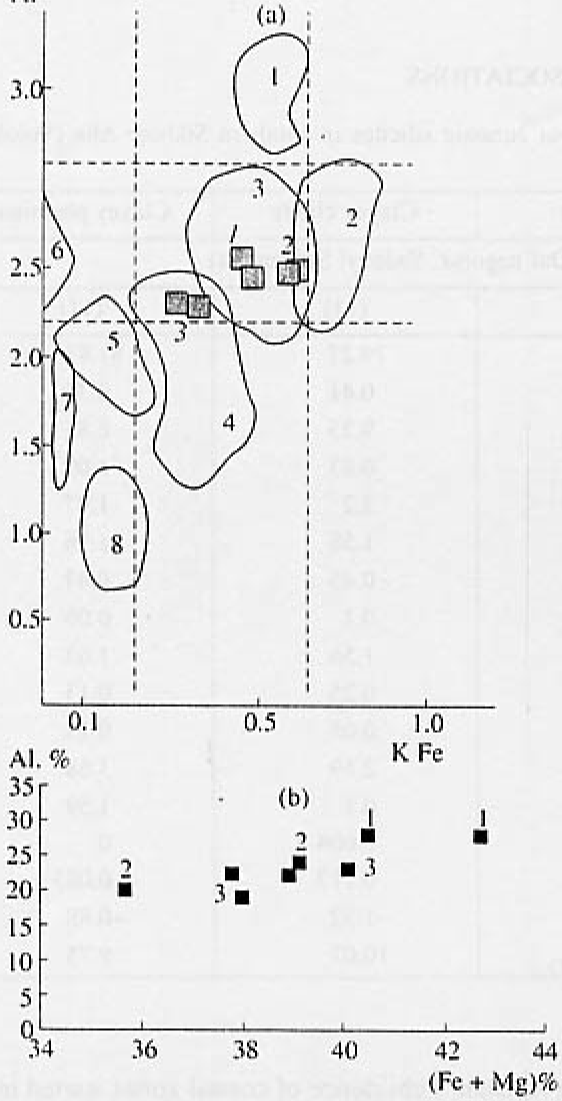

Fig. 6. Distribution of chlorite types versus Fe and Al contents. (a) Crystallochemical pattern of polygenous chlorites from siliceous rocks of the Rudnaya River section (diagram fields are given after Drits and Kossovskaya, 1991). (*1*) chlorites from Olenekian cherts (Sample 19/30), (2) chlorites from Norian cherts (Sample 19/64), (*3*) chlorites from Rhaetian clay-poor siliceous rocks (Sample 19/77). Numerals denote the following fields: (1) di- and trioctahedral Al–Fe–Mg-chlorite, (2) Fe-chlorite from iron ores, (3) Fe–Mg-chlorite from clastogenic formations, (4) Fe–Mg- and Mg-chlorites from basic magmatic rocks, (5) Mg-chlorite from evaporite formations, (6) Mg-chlorite from halite and Mg–K salts of basins with a high degree of salinization, (7) Mg-chlorite from ophiolite, (8) Mg-chlorite from kimberlite. (b) Al vs. (Fe + Mg) plot for chlorites from Triassic cherts of the Dal'negorsk section along the Rudnaya River based on classification diagram in (Kossovskaya and Shutov, 1971). Numerals in the diagram: (1) chlorites from Olenekian cherts (Sample 19/30), (2) chlorites from Norian cherts (Sample 19/64), (3) chlorites from Rhaetian clay-poor siliceous rock (Sample 19/77).

postsedimentary transformation of rocks. The metamorphism grade of the analyzed rocks can also be established by the crystallinity index (IC) of micas (Kubler, 1967; Weaver *et al.*, 1984; and others), which is defined on the basis of the width of 10 Å peak of ethylenglycol-saturated illite sample at half-maximum (in mm). The IC value (IC = 2) in the clayey fraction of siliceous rocks from the Rudnaya River section does not vary from the Triassic to Aalenian and increases (IC = 3) only in the upper (Upper Jurassic–Lower Cretaceous) part of the section. The IC values testify that Triassic siliceous rocks reached the metagenetic stage, whereas the Upper Jurassic–Lower Cretaceous part of the section was less transformed (possibly, up to the initial stage of metagenesis).

Chlorite is another common mineral in the clayey fraction of siliceous rocks. Analysis of the composition of chlorites shows that they belong to Fe–Mg varieties of metagenetically altered rocks. Unfortunately, it is difficult to determine the composition of chlorites in Jurassic–Lower Cretaceous siliceous rocks due to their extremely fine size. In terms of crystallochemical characteristics, they occupy the following positions: chlorites in the Olenekian and Norian cherts fall into the field of Fe–Mg chlorites of clastogenic rocks, whereas chlorites in Rhaetian cherts fall into the field of chlorites from basic magmatic rocks (Fig. 6).

Thus, minerals from the terrigenous admixture in siliceous rocks underwent significant lithogenetic transformations together with host rocks. However, the degree of these transformations is not so high to obliterate primary sedimentary features of the rocks. Therefore, changes in the initial composition of the terrigenous admixture are manifested as the formation of more stable structural types of clay mineral associations, and the clay mineral parageneses are governed by the nature of adjacent continental provenances.

The chemical composition, mainly distribution of rare and trace elements, is one of the important parameters characterizing siliceous rocks (Table 3). Investigation of the chemical composition of siliceous rocks based on the concept of regular changes in the composition of oceanic water from continental margin to pelagic zones makes it possible to decipher sedimentation conditions and reveal specific features of the studied rocks. In Fig. 4 presented in (Adachi *et al.*, 1986), siliceous rocks of the Dal'negorsk section are shown as sedimentary rather than hydrothermal rocks. Regardless of the bulk concentration in rocks, the REE distribution in Triassic rocks is similar to that of PAAS. Such a distribution suggests the formation of clayey fraction owing to the erosion of sialic crust with biogenic material as a dilutor.

The chondrite-normalized REE composition of siliceous rocks displays a negative Eu anomaly (Fig. 5a), which is typical of all sedimentary rocks and indicator of the absence of hydrothermal components (Fig. 7). The Anisian siliceous rocks with slightly different

Table 3. Average chemical composition of Middle Triassic–Lower Jurassic silicites in southern Sikhote Alin (Volokhin, 1988, Table 5)

Components	Cherts	Phtanites	Clayey cherts	Clayey phtanites
	Rudnaya River (Dal'negorsk, Sadovyi Settlement)			
	(9)	(8)	(11)	(11)
SiO_2	91.88	91.6	79.27	81.85
TiO_2	0.09	0.09	0.41	0.32
Al_2O_3	3.16	2.83	9.25	6.81
Fe_2O_3	0.35	0.44	0.83	1.09
FeO	2.25	1.89	3.2	1.97
MgO	0.61	0.37	1.58	1.26
CaO	0.15	0.18	0.45	0.47
MnO	0.09	0.03	0.1	0.06
K_2O	0.39	0.56	1.56	1.63
Na_2O	0.07	0.07	0.25	0.13
P_2O_5	0.06	0.07	0.05	0.13
L.O.I.	0.57	1.35	2.59	3.68
C_{org}	0.09	0.28	0.1	1.59
C_{carb}	0.01	0	0.004	0
Al_2O_3/SiO_2	0.034	0.031	0.117	0.083
$FeO^*-0.578\ Al_2O_3$	0.77	0.69	−1.32	−0.88
$(FeO + MgO)/TiO_2$	29.89	26.22	10.07	9.75

Note: Number of analyzed samples is given in parentheses.

geochemical parameters are an exception. The lower Anisian rocks are characterized by a positive Tb anomaly and general enrichment in lREE. The middle Anisian rocks show a weak negative Ce anomaly, suggesting the accumulation of siliceous sediments away from the continental margin, i.e., in the pelagic zone. However, its low intensity and weak manifestation confined to Anisian rocks suggest that these rocks formed on an oceanic rise at the boundary with Ce-depleted deep waters.

RESULTS AND DISCUSSION

In the Early and Middle Triassic, the lowland situated west of the marine basin was marked by a well developed river network and homogeneously humid conditions. The evaporation rate was high and reached the maximum in the Late Triassic (Yasamanov, 1985). The principal type of landscape was represented by sylvan savanna with massifs of poor xerophyte vegetation. The denudated sialic complexes (acid crystalline rocks of the granitoid and metamorphic types) served as provenances. This is testified by the mica–chlorite association (with the predominant mica and subordinate Fe–Mg-chlorite of the clastogenic formation) in siliceous rocks. The chlorite content gradually increases or decreases. The mica/chlorite ratio irregularly changes in the Triassic and the chlorite content predominates by the Anisian. Subsidence of coastal zones started in the Middle Triassic and a large quantity of organic material concentrated in the coastal plain was delivered to the basin. Consumption of organic material was followed by the plankton death on a mass scale and intense Anisian anoxia in the basin. As a result, carbonaceous mudstone interlayers appeared in deep-water cherts, and horizons with a high content of radiolarians are recorded in the overlying siliceous rocks.

In the Late Triassic, the Primorye territory was characterized by subtropical climate with high temperature, humid condition, and high evaporation rate. Landscapes of highlands represented deserts, and vegetation grew only on flooded lowlands (Yasamanov, 1985). The formation of intrabasinal volcanic edifices and their subsequent destruction changed the terrigenous composition in siliceous rocks. Micaceous material gave way to chlorite in cherts in the terminal middle Anisian–Rhaetian. The maximum chlorite content is observed in Carnian and Norian rocks. Radiolarian shells were also filled with chalcedony approximately during this time interval (middle Anisian–Middle Jurassic). In addition, jaspers sandwiched between late Carnian basaltic flows contain radiolarian shells filled with lutecite. The content of radiolarian remnants is maximal in the late Carnian cherts, suggesting a high bioproductivity in this time interval. The onset of the

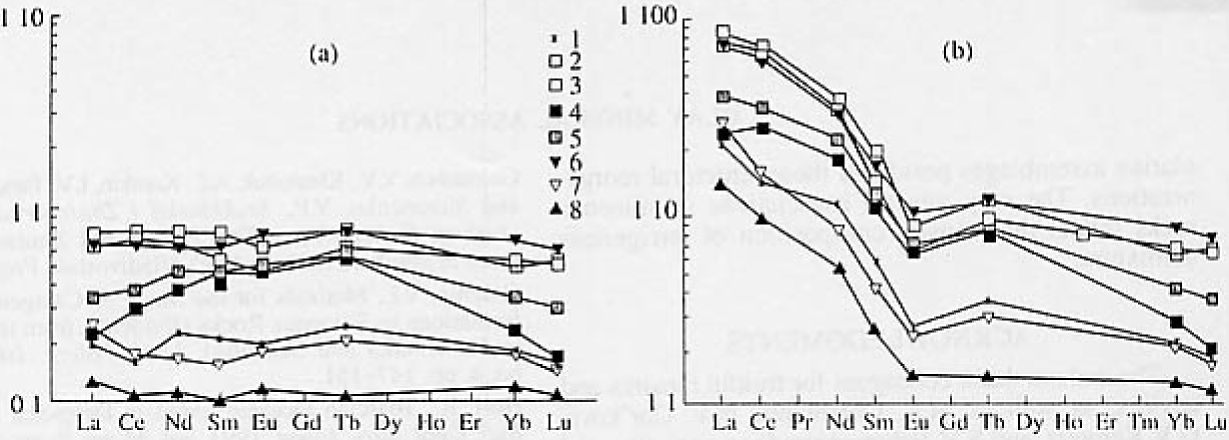

Fig. 7. REE distribution in siliceous rocks from the Dal'negorsk section along the Rudnaya River. (a) PAAS-normalized, (b) chondrite-normalized. Sample numbers after K.A. Krylov. (1) Upper Olenekian silicites (T_1o_2), Layer 4 (layer numbers as in Fig. 1), Sample 1002-3; (2) upper Olenekian silicites (T_1o_2), Layer 5, Sample 1011-4; (3) silicites from the contact between upper Olenekian and lower Anisian rocks, Layer 6, Sample 1011-8; (4) lower Anisian silicites (T_2a_1) at the contact with the carbonaceous horizon, Layer 6, Sample 1011-14; (5) lower Anisian silicites (T_2a_1) above the carbonaceous horizon, Layer 6, Sample 1011-15; (6) lower Anisian silicites (T_2a_1), the upper part of Layer 6, Sample 1011-32; (7) middle Anisian silicites (T_2a_2), the base of Layer 6, Sample 1011-38; (8) middle Anisian silicites (T_2a_2), the middle part of Layer 7, Sample 1011-42.

late Carnian basaltic volcanism could change geochemical conditions in the marine basin. This, together with the presence of organic material, could lead to the growth of plankton bioproductivity and its consequent dying off on a mass scale after the termination of the volcanic activity and onset of a new geochemical environment.

The region had a humid, moderately warm climate in the terminal Lias. In the Early–Late Jurassic, coal-bearing sediments accumulated in coastal zones periodically flooded by the sea. The marine basin received fresh water during the maximum transgression and a strongly inundated landscape developed in maritime zones. Supply of terrigenous material into the marine basin was minimum. As a result, the Rhaetian–Early Jurassic section is dominated by biogenic siliceous material with a very low content of clay constituent. An intense anoxic environment was developed at the beginning of the Early Jurassic. Like in the Anisian, the large-scale radiolarian bloom observed in this period (Table 2) was caused by the supply of organic material into the marine basin from coastal zones.

Paleogeographic conditions in the region drastically changed at the end of the Late Jurassic. The deep-water sedimentation gave way to the continental margin type. According to (Kemkin and Kemkina, 1998), the studied oceanic plate sector approached the accretion zone in the Late Cretaceous–Early Cretaceous and silica accumulation in the basin gave way to terrigenous sedimentation. Flyschlike terrigenous sediments with abundant smectite, chlorite, and mica started to accumulate in the basin. The number of radiolarian assemblages reduced. Unlike radiolarians from the underlying sequence, the preserved shell remnants are filled with smectite in the central part and cryptocrystalline quartz in the peripheral zone.

At the Jurassic/Cretaceous boundary, the Sikhote Alin region was characterized by subduction of the oceanic plate under the continental margin. However, evolution of the imbricate structure in the region was only completed in the Late Mesozoic. The Taukha terrane corresponds to the subduction zone (Khanchuk, 2001). The involvement of deep-water siliceous rocks in the accretionary complex in the Early Cretaceous, promoted the metagenetic alteration of siliceous rocks, recrystallization of radiolarian shells, and transformation of clay minerals into more stable varieties. However, clay mineral associations in cherts preserve specific features of the primary material. Shells are filled with chalcedony and smectite and chlorite appears in chert during a single time interval, suggesting a common source of their formation.

CONCLUSIONS

The change of clay mineral associations in siliceous rocks of southern Sikhote Alin coincides with large-scale replacements of radiolarian assemblages and is governed by paleogeographic, paleotectonic, and paleoclimatic conditions. Cherts of the Rudnaya River area formed in a deep-water environment in the Triassic–Lower Cretaceous, it happened at a moderate distance from the continental margin in the Triassic, and at the base of the continental rise in the Early Cretaceous.

Carbonaceous horizons of the Triassic–Lower Cretaceous section along the Rudnaya River mark significant structural reorganizations in the region. Changes of clay mineral associations and replacement of radiolarian assemblages postdated these structural reorganizations. The clay mineral associations in siliceous rocks reflect the primary composition of terrigenous admixture.

ACKNOWLEDGMENTS

The authors thank colleagues for fruitful remarks and advices, as well as M.E. Gorshkova, N.V. Gor'kova, G.V. Karpova, and E.V. Pokrovskaya for preparation and laboratory treatment of the analyzed samples.

This work was supported by the Russian Foundation for Basic Research, project no. 00-05-64618.

REFERENCES

Adachi, M., Yamamoto, K., and Sugisaki, N., Hydrothermal Chert and Associated Siliceous Rocks from the Northern Pacific–Their Geological Significance as Indications of Ocean Ridge Activity, *Sediment. Geol.*, 1986, vol. 47, no. 1/2, pp. 125–148.

Bragin, N.Yu., *Radiolyarii i nizhnemezozoiskie tolshchi Vostoka SSSR* (Radiolarians and Late Mesozoic Sequences in the Eastern Soviet Union), Moscow: Nauka, 1991.

Bragin, N.Yu., Triassic Radiolarian Zones in the Russian Far East, *Stratigr. Geol. Korrelyatsiya*, 2000, vol. 8, no. 6, pp. 59–73.

Bragin, N.Yu. and Krylov, K.A., Carboniferous Rock Horizons in Triassic and Late Jurassic Cherts in the Stratotype of Russian Far East (Primorye), *Stratigr. Geol. Korrelyatsiya*, 2002, vol. 10, no. 5, pp. 85–91.

Bragina, L.G., Ben'yamovskii, V.N., and Zastrozhnov, A.S., Upper Cretaceous Radiolarians, Foraminifers, and Stratigraphy in the Southeastern Russian Platform (Right Bank of the Volga River, Volgograd Region), *Stratigr. Geol. Korrelyatsiya*, 1999, vol. 7, no. 5, pp. 84–92.

Bralower, T.J., Sliter, W.V., Arthur, M.A., Leckie, R.M., Allard, D., and Schanger, S.O., Dysoxic/Anoxic Episodes in the Aptian–Albian (Early Cretaceous), *The Mesozoic Pacific: Geology, Tectonics, and Volcanism*, Geophysical Monograph 77, AGU Books Board, 1993, pp. 5–38.

Drits, V.A. and Kossovskaya, A.G., *Glinistye mineraly: slyuda, khlority* (Clay Minerals: Mica and Chlorites), Moscow: Nauka, 1991.

Gavrilov, Yu.O. and Kopaevich, F., Geochemical, Bioclimatic, and Biotic Consequences of Eustatic Fluctuations, *Stratigr. Geol. Korrelyatsiya*, 1996, vol. 4, no. 4, pp. 3–14.

Gavrilov, Yu.O., Kodina, L.A., Lubchenko, I.Yu., and Muzylev, N.G., The Late Paleozoic Anoxic Event Epicontinental Seas of Peri-Tethys and Formation of the Sapropelic Unit: Sedimentology and Geochemistry, *Litol. Polezn. Iskop.*, 1997, no. 5, pp. 492–517.

Gavrilov, Yu.O., Shchepetova, E.V., Baraboshkin, E.Yu., and Shcherbinina, E.A., The Early Cretaceous Anoxic Basin of the Russian Plate: Sedimentology and Geochemistry, *Litol. Polezn. Iskop.*, 2002, no. 4, pp. 359–380.

Golozubov, V.V. and Mel'nikov, N.G., *Tektonika geosinklinal'nykh kompleksov yuzhnogo Sikhote-Alinya* (Tectonics of Geosynclinal Complexes in Southern Sikhote Alin), Vladivostok: Inst. Tikhookean. Geol. Dal'nevostochn. Nauch. Tsentra Akad. Nauk SSSR, 1986.

Golozubov, V.V., Khanchuk, A.I., Kemkin, I.V., Panchenko, I.V., and Simanenko, V.P., *Taukhinskii i Zhuravlevskii terreiny (Yuzhnyi Sikhote-Alin)* (The Taukha and Zhuravlevka Terranes in Southern Sikhote Alin), Vladivostok: Preprint, 1992.

Grechin, V.I., Methods for the Study of Catagenetic Transformations in Siliceous Rocks (Evidence from the Miocene in Kamchatka and Sakhalin), *Litol. Polezn. Iskop.*, 1972, no. 4, pp. 147–151.

Hori, R., Toarcian Oceanic Event in Deep-Sea Sediments, *Bull. Geol. Surv. Japan*, 1993, vol. 44, no. 9, pp. 555–570.

Ishiga, H., Ishida, K., Dozen, K., and Musashino, M., Geochemical Characteristics of Pelagic Chert Sequences Across the Permian–Triassic Boundary in Southwest Japan, *The Island Arc*, 1996, no. 5, pp. 180–193.

Kaipov, A.D. and Levin, V.L., *Atlas mikrostruktur kremnistykh porod (kolchedannye mestorozhdeniya Kazakhstana)* (Atlas of Microstructures of Siliceous Rocks in Massive Sulfide Deposits of Kazakhstan), Alma-Ata: Nauka, 1982.

Kemkin, I.V. and Kemkina, R.A., The Jurassic–Early Cretaceous Biostratigraphy of Siliceous and Terrigenous Rocks in the Dal'negorsk Ore Region (Southern Sikhote Alin), *Tikhookean. Geol.*, 1998, vol. 17, no. 1, pp. 59–75.

Kemkin, I.V. and Khanchuk, A.I., Primary Data on the Early Cretaceous Accretionary Complex in the Chernaya River Basin (Southern Sikhote Alin), *Tikhookean. Geol.*, 1993, no. 1, pp. 140–143.

Khanchuk, A.I., Reconstruction of Early Cretaceous Transform Continental Plate Boundary in the Sea of Japan Region, Abstracts of Papers, *7 Mezhdunarodnaya konferentsiya po tektonike plit im. L.P. Zonenshaina* (7th Zonenshain Int. Conf. on Plate Tectonics), Moscow: Nauchnyi Mir, 1972, pp. 316–317.

Konstantinovskaya, E.A., The Early Cretaceous Marginal Sea of Kamchatka Peninsula, *Litol. Polezn. Iskop.*, 1997, no. 1, pp. 58–73.

Konstantinovskaya, E.A., Mesozoic Oceanic Siliceous, Carbonates, and Terrigenous Rocks in the Southeastern Taigonos Peninsula, Northeastern Russia, *Litol. Polezn. Iskop.*, 1998, no. 4, pp. 397–412.

Krasnyi, L.I. and Mikhailov, A.F., Siliceous–Volcanogenic Rock Formations in the Northwestern Pacific Mobile Belt, in *Osadochnye i vulkanogennye formatsii* (Sedimentary and Volcanogenic Rock Formations), Tr. Vses. Geol. Inst., Nov. Ser., 1966, vol. 128, pp. 132–140.

Kubler, B., Evaluation quantative du metamorphisme par la cristallinite de l'illite, *Bull. Cent. Rech. Pau SNPA*, 1968, vol. 2, pp. 385–397.

Kuhnt, W., Thurov, J., Wiemann, J., and Herbin, J.P., Oceanic Anoxic Conditions around the Cenomanian–Turonian Boundary and the Response of the Biota, *Mitteil. Geol. Paleontol.*, 1986, vol. 60, pp. 205–246.

Marcucci Passerini, M., Bettini, P., Dainelli, J., and Sirugo, A., The "Bonarelli Horizon" in the Central Apennines (Italy): Radiolarian Biostratigraphy, *Cretaceous Res.*, 1991, no. 12, pp. 321–331.

Markevich, P.V., *Flishevye formatsii severo-zapadnoi chasti Tikhookeanskogo skladchatogo poyasa* (Flysch Formations in the Northwestern Pacific Foldbelt), Moscow: Nauka, 1978.

Markevich, P.V. and Konovalov, A.I., *Nizhnemelovye obrazovaniya Sikhote-Alinya* (Lower Cretaceous Rocks in Sikhote Alin), Vladivostok: Dal'nauka, 1978.

Matsuoka, A., Hori, R., Kuwahara, K., *et al.*, Triassic–Jurassic Radiolarian-Bearing Sequences in the Mino Terrane, Central Japan, *Guide Book for Interrad VII Field Excursion*, Osaka, 1994, pp. 19–61.

Mazarovich, A.O., Tectonics of Southern Sikhote Alin, *Geotektonika*, 1981, no. 5, pp. 84–95.

Mazarovich, A.O., *Tektonicheskoe razvitie yuzhnogo Primor'ya v paleozoe i rannem mezozoe* (Paleozoic and Early Mesozoic Evolution of Southern Primorye), Moscow: Nauka, 1985, issue 392.

Mazarovich, A.O. and Rikhter, A.V., The Triassic Paleotectonics and Paleogeography of the Southern Russian Far East, *Geotektonika*, 1985, no. 6, pp. 74–85.

Natal'in, B.A., The Mesozoic Accretion and Collision Tectonics in the Southern Far East of the Soviet Union, *Tikhookean. Geol.*, 1991, no. 5, pp. 3–23.

O'Dogherty, L., Biochronology and Paleontology of the Mid-Cretaceous Radiolarians from Northern Apennines (Italy) and Betic Cordillera (Spain), *Mem. Geol.*, 1994, no. 21.

Shutov, V.D., Classification of Terrigenous Rocks and Graywackes, *Grauvakki* (Graywackes), Moscow: Nauka, 1972, pp. 9–29.

Volokhin, Yu.G., Clay Minerals in Paleozoic and Mesozoic Geosynclinal Siliceous Rocks of the Southern Far East, *Geokhimiya i petrokhimiya osadochnykh kompleksov Dal'nego Vostoka* (Geochemistry and Petrochemistry of Sedimentary Complexes in the Russian Far East), Vladivostok: Dal'nevostochn. Nauchn. Tsentr Akad. Nauk SSSR, 1980, pp. 76–99.

Volokhin, Yu.G., *Kremnevye porody Sikhote-Alinya i problema proiskhozhdeniya geosinklinal'nykh kremnevykh tolshch* (Siliceous Rocks in Sikhote Alin and Origin of Geosynclinal Siliceous Sequences), Vladivostok: Dal'nevostochn. Vost. Nauch. Tsentr Akad. Nauk SSSR, 1985.

Volokhin, Yu.G., Geochemical Criteria for the Correlation of Siliceous Sequences and Paleogeographic Reconstructions, *Litol. Polez. Iskop.*, 1988, no. 3, pp. 64–81.

Volokhin, Yu.G., Burii, G.I., Rudenko, V.S., and Mikhailik, E.V., The Mesozoic Siliceous Formation of Sikhote Alin, *Tikhookeanskaya okraina Azii. Geologiya* (The Pacific Margin of Asia: Geology), Moscow: Nauka, 1989, pp. 95–106.

Volokhin, Yu.G., Burii, G.I., Rudenko, V.S., and Filippov, A.N., The Triassic Siliceous Formation in Southern Sikhote Alin, *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1990, no. 4, pp. 45–57.

Weawer, C.E., Broekstra, B.R., Highsmith, P.B., *et al.*, Shale-Slate Metamorphism in Southern Appalachians, *Developments in Petrology*, Amsterdam: Elsevier, 1984, vol. 10.

Yamakita, S., Kadota, N., Kato, T., *et al.*, Confirmation of the Permian/Triassic Boundary in Deep-Sea Sedimentary Rocks; Earliest Triassic Conodonts from Black Carbonaceous Claystone of the Ubara Section in the Tamba Belt, *Southwest Japan*, 1999, vol. 105, no. 12, pp. 895–898.

Yasamanov, N.A., *Drevnie klimaty Zemli* (Ancients Climates of the Earth), Leningrad: Gidrometeoizdat, 1985.

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