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The Permian–Triassic Crisis in the Biosphere as Manifested in the Paleo-Pacific Deep-Water Sequences

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Abstract—The deep-water successions in Japan, Sikhote-Alin, and Nevada demonstrate a sharply decreased silica productivity across the Permian–Triassic boundary, accumulation of carbonaceous shales, and virtually absolute absence of fossil radiolarians and sponges. In Japanese sections, this stratigraphic level is enriched in titanium, phosphorus, and yttrium, and also demonstrate a sharp decline in cerium content relative to other rare-earth elements. These phenomena are directly or indirectly related to the biotic crisis at the Permian–Triassic boundary. The geochemical anomalies are interpreted as related to significant environmental changes in response to intense tectonic activity. The changes caused extinction of many marine biotic groups, including siliceous plankton, and increased the primary productivity of lower phytoplankton taxa. The event in question differs from the Mesozoic anoxic episodes in its origin, significance, and duration, being followed by the well-manifested biotic crisis.

Key words: Permian, Triassic, extinction, radiolarians, sponges, phytoplankton, biogenic silica production, geochemistry, carbon, rare-earth elements, anoxia, Paleo-Pacific.

The Phanerozoic biotic crises, including the most significant one at the Paleozoic–Mesozoic boundary, are under intense study at present. According to available data, the last one affected all groups of marine biota and resulted in the unprecedented mass extinction of genera and families. In addition to biotic events, different geochemical anomalies that have been considered as related to the crisis are recognized near the Permian–Triassic boundary. Up to the present time, investigations were focused mainly on the Paleozoic–Mesozoic boundary shallow-water sections. Their results are now essentially supplemented with data on the concurrent deep-water deposits that is discussed below.

Upper Paleozoic and Mesozoic siliceous deposits are widespread in all structures framing the Pacific. Nevertheless, siliceous beds across the Permian–Triassic boundary have been recognized only recently, and study on them just have been started. Results of the study are greatly valuable first for understanding of deep-water sedimentation during the Paleozoic–Mesozoic transition, which is absolutely unknown as yet, and second, for a new interpretation of causes and character of the Late Paleozoic crisis in the biosphere. The Permian–Triassic boundary deposits of deep-water origin are known in few land areas: Sikhote-Alin, Japan, South China, British Columbia, and Nevada. However, the sections studied show closely similar biostratigraphic and lithological features suggesting a uniform and regular structure of this stratigraphic interval in the Paleo-Pacific deep-water sections.

In the Sikhote-Alin, the most complete Lower Triassic deep-water section is known near the Dal'negorsk Settlement (Figs. 1 and 2). It characterizes the lower part of the Triassic–Lower Jurassic reference section of siliceous deposits in eastern Russia (Bragin *et al.*, 1988; Bragin, 1991, 1993). The Triassic deposits of the section are thrust over the Lower Cretaceous sandstones and are represented from the base upward by the following beds (the modified description after Bragin *et al.*, 1988):

(1) Black and dark gray carbonaceous shales with interbeds of gray siliceous mudstones (apparent thickness 3 m).

(2) Siliceous mudstones light bluish gray when fresh and rusty-brown to black when weathered. The rocks are massive, schistose, and rich in sulfides. In the upper part of the bed, there are few interbeds of black schistose carbonaceous mudstone and light gray chert (5 m).

(3) Light gray flaggy and dense, weakly siliceous mudstone with interbeds (1 or 2 cm) of light gray glassy cherts translucent and bearing conodonts *Neospathodus waageni* Sweet and *N. pakistanensis* Sweet of the early Olenekian (Smithian) age. The chert interbeds also contain abundant siliceous sponge spicules and single spherical specimens of undeterminable radiolarians (5 m).

(4) Brick- to crimson-red and black carbonaceous-siliceous mudstone intercalated with interbeds of light gray translucent chert. The bed contains conodonts *Neospathodus triangularis* (Bender) and *N. homeri*

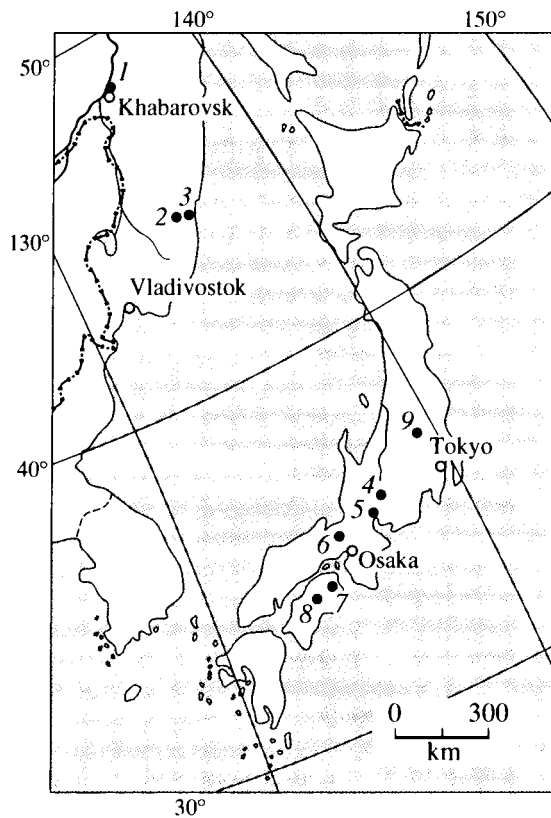


Fig. 1. Main Lower Triassic deep-water sections in Sikhote-Alin and Japan: (1) Khabarovsk; (2) Dal'negorsk; (3) Sadovyi; (4) Inuyama; (5) Kinkazan; (6) Sasayama; (7) Tenjinmaru; (8) Nakaoi; (9) Motegi.

(Bender) characteristic of the Upper Olenekian (Spathian) Stage and radiolarians *Cryptostephanidium longispinosum* (Sashida), *Pseudostylosphaera fragilis* (Bragin), *P. sp.*, and *Parasepsagon sp. cf. leptaleus* Sugiyama. Conodonts coexist with reworked Late Permian radiolarians *Follicuculus sp.* and siliceous sponge spicules (5 m).

(5) Gray siliceous mudstone with rare intercalations of light gray translucent cherts. Conodonts *Neospathodus homeri* (Bender) and *N. spathi* Sweet of the upper Olenekian (upper Spathian) Stage and radiolarians *Cryptostephanidium longispinosum* (Sashida), *Pseudostylosphaera fragilis* (Bragin), *P. sp.*, *Parasepsagon sp. cf. Leptaleus* Sugiyama, and *Oertlispongia sp.* are detected in the bed (2 m).

Above the beds, there are lower Anisian deposits represented by flaggy cherts with subordinate interbeds of siliceous mudstones. The deposits contain abundant radiolarians characteristic of the entire *Hozmadia gifuensis* Zone (Bragin, 1991; Sugiyama, 1992).

The Lower Triassic deep-water deposits in other Sikhote-Alin areas demonstrate similar composition. For example, to the southeast of Dal'negorsk, near the Sadovyi Settlement (Bragin, 1991), the basal part of the section is composed of gray and dark gray siliceous

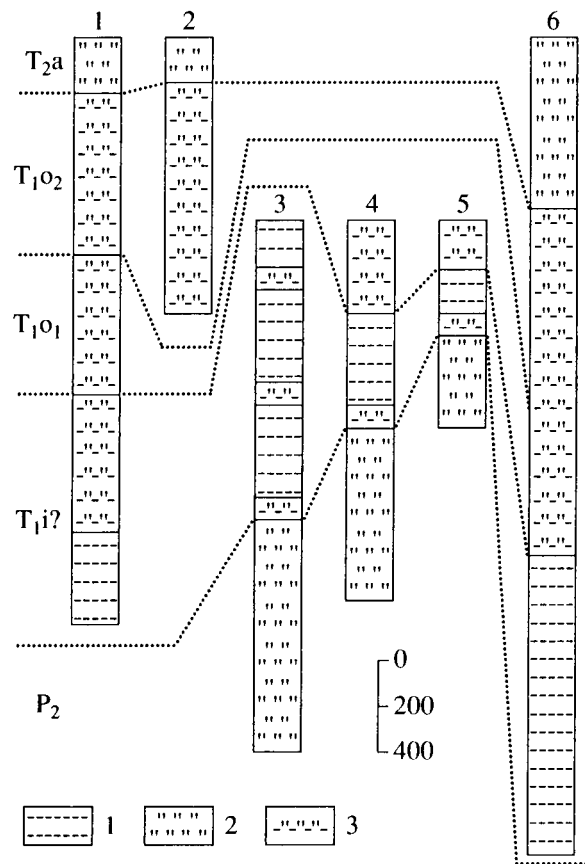


Fig. 2. Succession and correlation of the main Upper Permian–Lower Triassic deep-water deposits of Sikhote-Alin and Japan: (1) carbonaceous shale; (2) chert; (3) siliceous-clayey deposits.

(1) Dal'negorsk; (2) Sadovyi; (3) Nakaoi; (4) Tenjinmaru; (5) Sasayama; (6) Kinkazan. Symbols for stratigraphic units: P₂, Upper Permian; T₁i?, presumable Lower Triassic, Induan Stage; T₁o₁, Lower Triassic, lower Olenekian Stage; T₁o₂, Lower Triassic, upper Olenekian Stage; T₂a, Middle Triassic, Anisian Stage.

mudstones up to 10 m thick. The mudstones yield the late Olenekian (Spathian) conodonts *Neospathodus triangularis* (Bender) (Figs. 1 and 2). In the Khabarovsk region, on the right bank of the Amur River near the railway bridge (Bragin, 1991, 1992), the Lower Triassic deposits in a tectonic block are presumably 20 m thick (the thickness may be overestimated because of folding) and represented by alternating gray beds of siliceous mudstone and clayey chert bearing the late Olenekian (Spathian) conodonts *Neospathodus triangularis* (Bender), *N. homeri* (Bender), and *N. spathi* Sweet (Fig. 1). According to lithological and biostratigraphic features, these deposits can be correlated to beds 2 and 3 of the Dal'negorsk section. Similarly to the Dal'negorsk section, the Khabarovsk and Sadovyi sections predominantly consist of clayey Lower Triassic deposits overlain by the Anisian radiolarian cherts.

Several Upper Permian–Lower Triassic deep-water sections are known in Japan. In the Shikoku Island, the

Nakaoi section (Kakuwa, 1996a, 1996b) exhibits the following beds (Figs. 1 and 2):

(1) Gray flaggy chert with radiolarians (*Neoalballiella optima*) characteristic of the Dzhulfian Stage and lower Dorashamian Substage (9 m).

(2) Gray clayey chert of the upper Dorashamian Substage with conodonts *Neogondolella chanxingensis* and *N. subcarinata* (0.5 m).

(3) Black carbonaceous shale with horizons of gray siliceous mudstone (up to 15 m thick).

Bed 3 of the section is supposed to be of Lower Triassic (Induan) age, but paleontological remains are missing here. The bed is similar in lithology to the basal carbonaceous deposits of the Dal'negorsk section.

In the Tenjinmaru section of the eastern Shikoku Island (Kakuwa, 1996a, 1996b), the following deposits are described (Figs. 1 and 2):

(1) Gray flaggy cherts with radiolarians *Neoalballiella optima* of the Dzhulfian Stage and lower Dorashamian Substage (8 m).

(2) Gray chert with intercalations of gray mudstone bearing conodonts *Neogondolella changxingensis* and *N. subcarinata* of the upper Dorashamian Substage (1.5 m).

(3) Black carbonaceous shale (1.5 m).

(4) Black carbonaceous shale with interbeds of gray dense siliceous mudstone (1.5 m).

(5) Gray massive siliceous mudstone with rare interbeds of gray chert; the rocks yield conodonts *Neospathodus waageni* Sweet, *N. dieneri* Sweet, and *N. conservativus* Sweet peculiar to the lower Olenekian (lower Smithian) Substage (4 m).

The data suggests that the member of carbonaceous shales (Bed 3 of the Nakaoi section and beds 3 and 4 of the Tenjinmaru section) corresponds to the stratigraphic interval from the uppermost Dorashamian to the lowermost Olenekian. Most likely it is of the Induan (Griesbachian–Dienerian) age. The lower Olenekian deposits (Bed 5) of the Tenjinmaru section are similar in lithology to coeval deposits of the Dal'negorsk section.

In the Honshu Island, analogous sections are known to the north of Osaka (the Sasayama section), in the Gifu area (the Kinkazan and Inuyama sections), and to the north of Tokyo in the Ashio Mountains (the Motegi section). In the Sasayama section (Ishiga *et al.*, 1996), the 5-m-thick bed of gray Dzhulfian–Dorashamian chert is overlain by the following succession attributed to the Early Triassic (Figs. 1 and 2):

(1) Dark gray siliceous mudstone (0.5 m).

(2) Black carbonaceous mudstones (0.8 m).

(3) Mudstone with intercalations of siliceous mudstone (1 m).

Permian deposits are missing in the Kinkazan section (Sugiyama, 1992), where the bed succession (from the base upward) is as follows (Figs. 1 and 2):

(1) Black carbonaceous shale (up to 20 m thick).

(2) Dark gray and gray siliceous-clayey shales (up to 15 m thick).

(3) Dark gray and black clayey cherts with abundant redeposited clasts of Permian cherts ranging in size from meter-scale blocks to microinclusions (up to 10 m).

Bed 1 contains no fossils other than single Permian radiolarians, which are evidently reworked. The upper part of Bed 2 and the lower part of Bed 3 yielded the Early Triassic (late Olenekian) assemblage of conodonts and radiolarians. The upper part of Bed 3 contains the early Anisian microfauna; Bed 4 is of the middle Anisian age (Sugiyama, 1992). The section thickness is likely overestimated because of tectonic doubling in some members.

In the Inuyama section (Fig. 1) accepted as the reference section of the Triassic–Jurassic deep-water deposits of Japan (Matsuoka *et al.*, 1994), the Lower Triassic part is represented by greenish gray siliceous-clayey shales with frequent interbeds of black carbonaceous mudstone and light gray dolomite; the total apparent thickness is 10–15 m. These deposits contain Olenekian conodonts *Neospathodus waageni* Sweet and *N. homeri* (Bender). Above, there are Anisian radiolarian cherts. Lithological composition of all rock types in the section has been thoroughly studied (Matsuoka *et al.*, 1994). The siliceous-clayey shales are composed of quartz microgranules and clay minerals. The black mudstones are enriched in carbon and carbonates. The dolomites consist of rhombohedral dolomite crystals also dispersed in other rock types. Similar deposits are widespread in adjacent areas of Japan (the Mino, Chichibu, and Northern Kitakami belts), where they are known as the facies of the “Toishi-type Shale” (Imoto, 1984; Ishida *et al.*, 1992; Sashida *et al.*, 1992; Saito, 1993). On the basis of conodonts, these deposits are attributed to the Olenekian (Smithian and Spathian) Stage (Koike, 1981). They are well correlated with coeval deep-water deposits of the Sikhote-Alin, to be exact, with beds 1–3 of the Dal'negorsk section.

In the Motegi section (Fig. 1), the Upper Permian gray cherts are overlain by black carbonaceous shales (up to 2 m) of the lowermost Triassic (?) and by gray siliceous mudstones (1 m) presumably of the Olenekian age, which are similar in lithology to “the Toishi type Shale” (Kamata and Kajiwarra, 1996). The Motegi section shows an insignificant thickness of the Lower Triassic deposits.

In the East Pacific framing structures, deep-water deposits of the Lower Triassic were recognized in the Quinn River section, Nevada (Blome and Reed, 1995). The section begins with Upper Permian deposits. The Dzhulfian Stage (radiolarians of the *Neoalballiella optima* Zone) is represented by flaggy cherts. The Dorashamian Stage (radiolarians of the *Neoalballiella ornithiformis* Zone) corresponds to mudstone beds with rare horizons of black carbonaceous shales. The Induan Stage has not been recognized in the Quinn

River section. The presumable lower Olenekian Stage is represented by carbonaceous shales alternating with mudstones devoid of fossils. The upper Olenekian deposits with radiolarians *Parentactinia nakatsugawaensis* and the lower Anisian deposits with radiolarians *Hozmedia gifuensis* form the interval of alternating beds of siliceous mudstone and chert. Sections of similar type are known in the British Columbia (Isozaki, 1997) and were recently found in southern China (A. Yao, personal communication).

Other sections of Lower Triassic deep-water deposits have not been found as yet. Nevertheless, the available material is sufficient for outlining some regular compositional features of the Paleo-Pacific deep-water sections: (1) absence of the lowermost Triassic siliceous deposits; (2) gradual replacement of terrigenous deposits by siliceous upper Olenekian–lower Anisian sediments; and (3) abundance of carbonaceous shales in the lowermost Triassic interval, which become rapidly thinning upward and completely disappear in the lowermost Middle Triassic. These features are typical of all the sections described and, undoubtedly, characterize the history of the Paleo-Pacific deep-water sedimentation that was closely related to the global biotic and abiotic events at the Late Permian–Early Triassic transition.

It is very significant that the biogenic silica production ceased or noticeably diminished in the Early Triassic. In Japan, Sikhote-Alin, and many other regions, the Permian and Middle–Upper Triassic deep-water deposits are represented by facies of radiolarian cherts showing composition and structure persistently uniform in lateral directions and accumulated during a long period of time. The facies turned out to be untypical of the Early Triassic time, and absence of relevant beds in the sections is not associated with signs of regression and increased supply of clastic material, or with other indications suggesting changes in the bathymetry and morphology of sedimentary basins. The phenomenon can be reasoned only in terms of biotic crisis and degradation of siliceous plankton (radiolarians) that resulted in a sharp decline of biogenic silica production.

There are many facts confirming this inference. First, the biogenic origin of radiolarian cherts was established by many investigators (Vishnevskaya, 1984; Volokhin, 1985; Kaleda, 1987). In particular, the biogenic origin of SiO_2 of the Middle Triassic–Lower Jurassic siliceous deposits of the Inuyama section was revealed by the chemical and X-ray structural analyses (Matsuoka *et al.*, 1994). Second, in Japan and Sikhote-Alin, black shales of the presumable Induan age and siliceous mudstones of the lower Olenekian Substage contain no radiolarians other than the reworked Permian forms and similar spherical forms, which have not been identified as yet and probably belong to the order Entactinaria (Bragin, 1991; Sugiyama, 1992). Finally, sections of shallower deposits in different regions of the world are also characterized by the extremely poor

radiolarian assemblages of the Early Triassic age. The oldest Triassic radiolarians are known from the upper Induan–lower Olenekian (Dienerian–lower Smithian) deposits of northwestern Turkey. They were found in dark gray and black limestones in association with conodonts, such as the late Induan *Neospathodus dieneri* Sweet and *Clarkina procerocarinata* Kozur, and the latest Induan–early Olenekian *N. dieneri* Sweet and *N. conservativus* (Muller) (Kozur *et al.*, 1996). Only three radiolarian species represented by *Entactinia (Stigmospaerostylus) turkensis* (Kozur, Kaya et Mostler) and simple spherical spumellarians were found in these rocks. Younger (Late Olenekian or Spathian) radiolarian assemblages known from Japan, Thailand, and Sikhote-Alin also show the low diversity and predominance of primitive Entactinaria forms. Rare representatives of Mesozoic Nassellaria and Spumellaria are represented by primitive species in this case (Sashida, 1983, 1991; Bragin, 1991; Sugiyama, 1992; Sashida and Igo, 1992; Nagai and Mizutani, 1993; Kamata, 1995). All characteristic Permian taxa with advanced morphology are already lacking in the Lower Triassic deposits (Bragin, 1991; Kozur *et al.*, 1996).

Thus, many radiolarian taxa became extinct, and radiolarian plankton degraded in the Early Triassic time that is manifested as cessation of deep-water biogenic silica accumulation in the Paleo-Pacific region. To better elucidate this phenomenon, it is necessary to investigate in detail the eastern Mediterranean foldbelt (Tibet, southeastern Asia), where the Permian and Middle–Upper Triassic siliceous deposits are well known, but Lower Triassic beds have not been recognized. According to the taxonomic composition, the known radiolarian assemblage from Tibet that was originally dated back to Early Triassic (Feng, 1992; Feng and Liu, 1993) is, in fact, of the Middle Triassic (late Anisian–early Ladinian) age (Kozur *et al.*, 1996). As far as the Mediterranean region proper is concerned, the biogenic silica accumulation of the Permian–Early Triassic time is not recorded there, and sediments of the deepest settings are represented by clays and micritic limestones (Kozur, 1993, 1995a, 1995b).

The facts presented above motivate reconsideration of one of sedimentological problems, namely, the relation between biogenic silica accumulation and volcanism. Previous attempts were aimed to synchronize episodes of biogenic silica accumulation and volcanic activity (Zhamoida, 1992). The Permian and Triassic are known as periods of worldwide active volcanism of the trap-type in platforms and rift-related belts and adjacent areas. However, the biogenic silica accumulation did not proceed throughout the Early Triassic. The discontinuation in silica accumulation cannot be evidently correlated with the secular variations in volcanic activity and was certainly associated with other factors. This is an important argument in favor of genetic disconnection of volcanism and silica accumulation, as stated earlier (Bragin, 1991).

The dynamics of cessation and recommencement of biogenic silica accumulation is of great interest. The studied sections show that both events were not instantaneous or extraordinary. On the contrary, they were intermittent and gradual. For instance, the intensity of Late Permian silica accumulation in the Tenjinmaru and Nakaio sections was analyzed using the so-called Ishiga diagram (Kakuwa, 1996a), where abscissa depicts the cumulative thickness of shale or mudstone interbeds in the siliceous sequence, and ordinate shows difference in the thickness of particular siliceous bed and the average thickness of cherty beds (Ishiga, 1994a). The analysis showed that the silica accumulation in the Tenjinmaru and Nakaio sections decreased in the late Dzhulfian time and grew again in the Dorashamian age. The Upper Permian section of Central Japan (the Mino and Tamba belts) also demonstrates the reduction of silica accumulation and replacement of radiolarian siliceous deposits by mudstones within the upper part of the Dzhulfian Stage (Kuwahara and Ezaki, 1994). Thus, the late Dzhulfian time marks the first episode of diminishing and short-time interruption of silica accumulation prior to its complete cessation in the early Triassic.

The cease of biogenic silica accumulation in the Early Triassic was evidently not instantaneous. In the Sasayama section of southwestern Japan, for example, black carbonaceous mudstones with low SiO₂ content overlie a thin horizon of gray siliceous mudstones (Ishida *et al.*, 1992; Ishiga, 1994b) thus evidencing gradual changes in sedimentation. In many sections, black mudstone beds occur at the base of the Lower Triassic sequence and are devoid of siliceous interbeds or siliceous fossils, except the scarce and small spherical forms conventionally attributed to radiolarians (Kozur *et al.*, 1996).

In the early Olenekian time, the deposition of black carbonaceous mudstones was succeeded by accumulation of siliceous mudstones known in Japan (the Toishit-type Shale) and Sikhote-Alin. The lower Olenekian deposits of the Dal'negorsk section include numerous, though thin interbeds of flaggy cherts (Bragin, 1991). However, these cherts do not correspond to true radiolarites, because they contain only rare spherical remains of these organisms, but bear abundant spicules of siliceous sponges, which were evidently the rock-forming components.

Being abundant but not diverse, the spicules represented only Hexactinellida megascleres of the order Lyssakinosa (Plate). Skeleton of these sponges consisted of disconnected megascleres (Rigby, 1995). Pentactines, including those with straight and curved paratangential rays, are most common, while hexactines and stauractines are less frequent.

This sponge assemblage is similar in composition to assemblages from the upper Induan–lower Olenekian strata of Turkey (Kozur *et al.*, 1996) and from the upper Olenekian beds of western United States (Rigby and

Ganey, 1983). The extremely low diversity of the oldest Mesozoic sponge assemblages can be explained by the crisis experienced by these organisms also at the Permian–Triassic boundary. The lowest, highly siliceous interbeds of the Triassic sections in the Sikhote-Alin and Japan were formed owing to the biogenic silica production by sponges, whose life activity begun before the restoration of radiolarian plankton productivity.

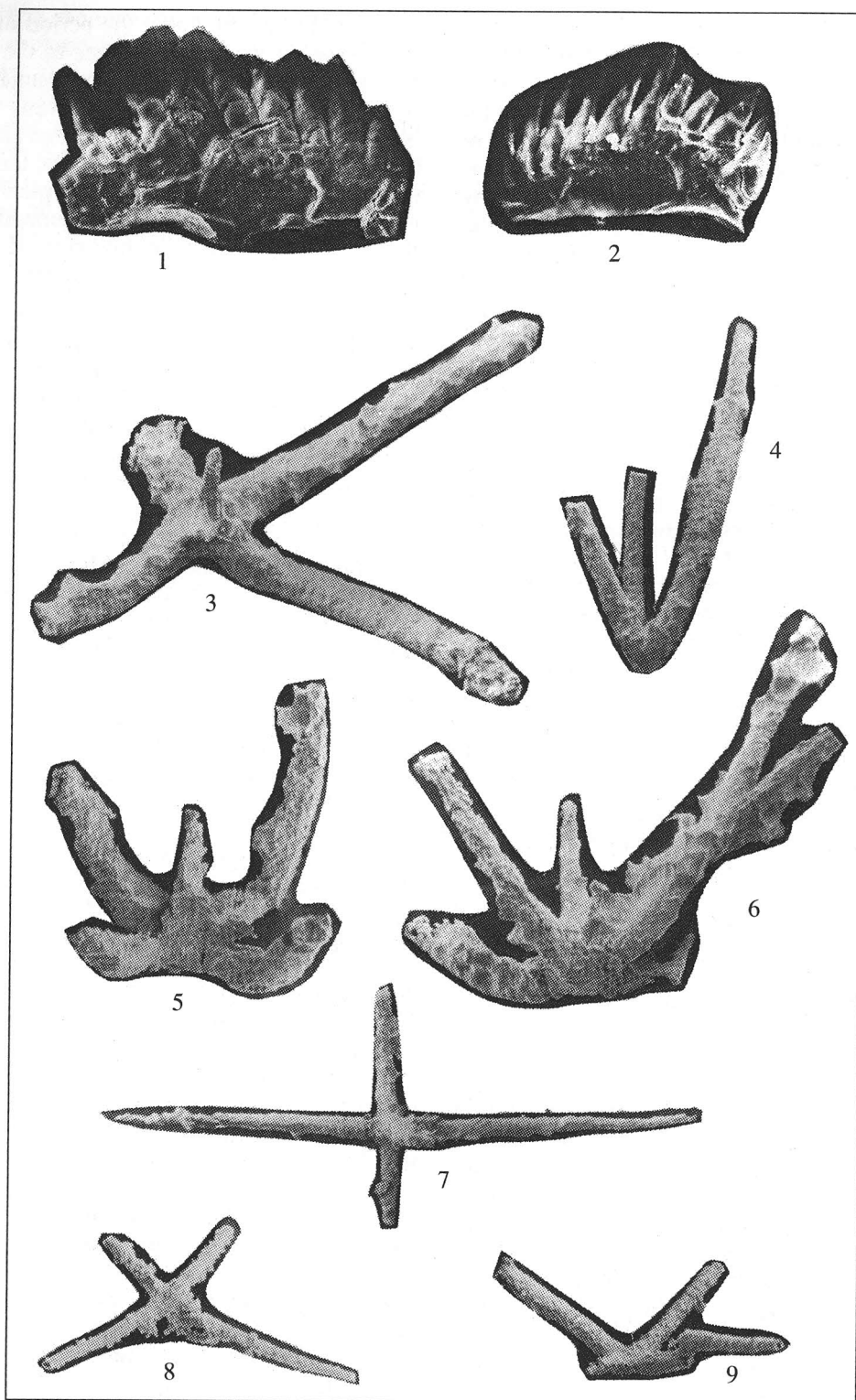
The Upper Olenekian deposits in Sikhote-Alin and Japan are also dominated by siliceous mudstones having low silica content and intercalated with frequent highly siliceous interbeds containing abundant spicules of siliceous sponges in association with radiolarian remains. True radiolarites occur locally. They become predominant higher in the section. The recommencement of biogenic silica accumulation that was interrupted in the earliest Triassic was a long gradual process. First signs of the true biogenic silica accumulation are confined to the basal Olenekian deposits in Sikhote-Alin and Japan, where siliceous components were produced by sponges (Kakuwa, 1996b). Radiolarians became again the rock-forming components in the late Olenekian time. The complete restoration of biogenic silica accumulation was in the early Middle Triassic.

The mentioned facts indicate that the discontinuation in the biogenic silica accumulation in the Paleopacific deep-water areas was a manifestation of the crisis in marine biological systems during the Late Permian–Early Triassic transitional time. In addition to the absence of siliceous sediments, the sections studied demonstrate other records of this biotic crisis, which are equally remarkable.

First of all, this is the occurrence of the Lower Triassic sediments rich in carbon. They represent persistent markers at the bases of all known Lower Triassic deep-water sections. Some carbonaceous interbeds can be also found higher in the sequence, for example, inside the upper Olenekian interval of the Dal'negorsk section. However, the interbeds are untypical of the Permian, Middle and Upper Triassic deposits of Japan and Sikhote-Alin.

There is another, lower Toarcian level of carbonaceous deposits in the Mesozoic siliceous successions of these regions. Study on the Lower Jurassic siliceous deposits in Japan revealed that this level corresponded to the global anoxic event (Jenkyns, 1988; Hori, 1990, 1992, 1993; Isozaki and Maruyama, 1992; Ishiga, 1993; Matsuoka *et al.*, 1994). The lower Toarcian carbonaceous deposits widespread in Japan and Sikhote-Alin (Bragin, 1993) are of siliceous type and yield abundant and diverse radiolarian assemblages: they also bear scattered pyrite crystals and concretions. Reworked Triassic conodonts were found at this level and immediately above it in different sections (Bragin, 1993; Matsuoka *et al.*, 1994).

Similarity and difference between the Lower Triassic and lower Toarcian carbonaceous deposits were



Characteristic fossils of the Olenekian Stage, the Dal'negorsk section

(1, 2) conodonts: (1) *Neospathodus waageni* Sweet, (2) *Neospathodus homeri* (Bender); (3-9) megascleres of siliceous sponges of the Lyssakinosa Order: (3, 5-7) pentactines, (4) unidentified fragment of a large megasclere, (8, 9) tetractines.

Magnification is $\times 90$ for all specimens.

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revealed by their comparative chemical analysis. The lower Toarcian cherts contain 0.5–2% of free carbon, and the C/N ratio varies here from 7 to 20 that is supposed to be a result of carbon generation by the metabolic activity of phytoplankton, whose remains were found in these deposits (Ishiga, 1993). The Lower Triassic carbonaceous mudstones are characterized by similar C/N isotopic ratio but the free carbon content in these rocks is much higher (2% and more) (Ishiga, 1993). Because the rocks do not yield paleontological remains, their carbon was suggested to be of the bacterial genesis. The suggestion is supported by the composition of hydrocarbons and free kerogen (Ishiga, 1993; Suzuki *et al.*, 1993).

Genesis of the Early Triassic carbonaceous deposition is a subject of discussions. Some researchers consider anoxic environments (Matsuoka *et al.*, 1994; Kakuwa, 1996a, 1996b; Kamata and Kajiwara, 1996) or even the “superanoxia” of the Early Triassic time (Isozaki, 1994, 1997) as controlling events. The anoxic environments are thought to be the cause of the mass extinction at the Permian–Triassic boundary (Wignall and Hallam, 1992, 1993; Wignall and Twitchett, 1996). Other researchers suppose that the Lower Triassic carbonaceous deposits accumulated in response to the disturbance of the oceanic water stratification and active upwelling of oxygen-deficient bottom water masses enriched in biologically active compounds (Kajiwara *et al.*, 1994; Ishiga *et al.*, 1996; Kakuwa, 1996a, 1996b).

There is an evident and significant difference between the supposed “superanoxia” of the Permian–Triassic transition time and other Mesozoic anoxic events, for example, of the early Toarcian or Cenomanian–Turonian interval. Mass extinctions like that at the Late Permian–Early Triassic boundary are untypical of the early Toarcian and Cenomanian–Turonian events. As far as radiolarians are concerned, their evolution during and immediately after the anoxic events was characterized by some interesting and surprising phenomena, for instance, by mass appearance of new taxa without any noticeable extinction of others (Kuhnt *et al.*, 1986; Thurow and Kuhnt, 1986; Hori, 1992; Matsuoka *et al.*, 1994; O’Dogherty, 1994) and by a sharp increase in siliceous plankton productivity. For example, the upper Cenomanian and lower Turonian deposits of the Mediterranean region include widespread beds of radiolarian cherts, which are frequently carbonaceous (lydites) or alternating with carbonaceous strata. These are known as the “Bonarelli Horizon” of Italy (Marcucci-Passerini *et al.*, 1991) and its analogues in the Betic Cordillera of Spain (O’Dogherty, 1994), and as the “Ananuri Horizon” of the Caucasus. Thus, data on radiolarians and biogenic silica accumulation at the Permian–Triassic boundary are incompatible with data characterizing the early Toarcian and Cenomanian–Turonian anoxic events

It should be added that the period of carbonaceous sedimentation was much longer in the Early Triassic than in the early Toarcian or Cenomanian–Turonian. In my opinion, the Early Triassic event was actually a “superanoxia”, as suggested by Isozaki (1993, 1994, 1997). In addition to the large scale, the Early Triassic anoxic event differs from other typical ones by some anoxia-related processes. Geochemical investigations of siliceous and other sections provide valuable information for understanding of the latter.

Geochemistry of the Upper Permian–Lower Triassic sediments was studied in different regions of the world. For example, the geochemical analysis of siliceous deposits has been started recently in Japan. In other countries, geochemical investigations were focused on carbonates of the relatively shallow genesis. As a result, significant geochemical changes were detected within this stratigraphic interval. These mutually correlatable changes correlative to other geological phenomena at the Paleozoic–Mesozoic boundary are of great significance for understanding the events of that time. The changes are manifested, first of all, in excursions of $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{34}\text{S}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ values.

The $\delta^{13}\text{C}_{\text{carb}}$ variations recorded in shallow-water carbonate sequences of the Alpine zone (Holser *et al.*, 1989, 1991) and Greenland (Oberhansli *et al.*, 1989) are very demonstrative. The $\delta^{13}\text{C}_{\text{carb}}$ value of 3.5‰ characterizing the Midian Stage (250 Ma) decreases to 2‰ in the upper Dzhulfian deposits (248 Ma). There was also a short positive excursion up to 3–3.2‰ (the lower Dorashamian Substage, 247 Ma) followed by the negative excursion down to –1‰ in the upper part of the stage (the Permian–Triassic boundary beds, 245 Ma old), which was particularly remarkable and rapid. Another positive $\delta^{13}\text{C}$ shift up to 0.5‰ (at the time of 244.5 Ma) was in the Griesbachian Stage, but the value declined again down to –0.5‰ in the upper part of the stage. Only after this last negative excursion, the value of $\delta^{13}\text{C}_{\text{carb}}$ increased again up to the high mid-Upper Permian level. Thus, the $\delta^{13}\text{C}_{\text{carb}}$ variation curve reveals three intervals of low values corresponding to the upper Dzhulfian Substage, Permian–Triassic boundary beds, and upper Griesbachian Stage of the Lower Triassic. These negative $\delta^{13}\text{C}_{\text{carb}}$ excursions mark periods of the declined productivity of marine biota. The first two intervals of low values coincide with two significant episodes of mass extinctions in the Late Permian (Stanley and Yang, 1994), and the third one corresponds to the earliest Triassic time of the lowest biota diversity and, correspondingly, of the low bioproductivity. The data are consistent with the rate of silica accumulation in Japan during the Late Permian–Early Triassic, where the silica accumulation first decreased at the end of the Dzhulfian Age, then grew in the Dorashamian time, and finally ceased at the Permian–Triassic boundary time (Kakuwa, 1996a).

Thus, the negative $\delta^{13}\text{C}_{\text{carb}}$ anomalies in the Mediterranean carbonate sections and events of decrease and

cessation of silica accumulation in the Pacific belt appear to be synchronous and can be interpreted as results of the low total productivity of marine biota. It seems that the occurrence of carbonaceous deposits in the Lower Triassic deep-water settings of the Pacific region contradicts this interpretation. However, carbon of these deposits is supposed to be the product of most primitive groups of phytoplankton, i.e., of bacteria or lower algae (Ishiga, 1993; Suzuki *et al.*, 1993; Ishiga *et al.*, 1994). The high primary productivity of this primitive microflora may oppress other groups of marine biota (Kakuwa, 1996a, 1996b). This may be the reason for the low restoration rates of radiolarian and other marine biotic communities during the Early Triassic (Alekseev, 1989; Hallam, 1991).

Another problem concerns the low $\delta^{13}\text{C}_{\text{carb}}$ value (-1%) in the Permian–Triassic boundary carbonates, which cannot be simply attributed to the decreased productivity of marine biota. There are two interpretations of this phenomenon: (1) oxidation of previously concentrated organic carbon as a result of extensive sea regression and emergence of shelf areas in the latest Permian (Holser and Magaritz, 1987; Baud *et al.*, 1989; Holser *et al.*, 1989, 1991); and (2) significant hydrological changes and upwelling of bottom water masses enriched in the light carbon isotope (Malkowskii *et al.*, 1989; Grotzinger and Knoll, 1995; Knoll *et al.*, 1996). Geochemical investigations of the Paleo-Pacific deep-water deposits can provide valuable information for solution of the problem.

These investigations were carried out in a series of Japanese sections. Geochemical results, when analyzed and compared to data on carbonaceous horizons accumulated during other Mesozoic anoxic events, for instance, during the early Toarcian or Cenomanian–Turonian ones, contribute much to understanding of biotic events near the Permian–Triassic boundary.

It was found out that the Lower Triassic mudstones of the Tamba and Chichibu groups are enriched in REE, U, and Ba being simultaneously depleted in Mn, Ca, and Sr (Musashito, 1993). Similar data were obtained by geochemical analysis of the Lower Triassic deposits of the Sasayama and Tenjinmaru sections, where they show, in addition, the high content of TiO_2 , P_2O_5 , Y, and some other components (Ishiga *et al.*, 1996).

TiO_2 is one of basic components of igneous rocks, and its high content in mudstones lacking pyroclastic admixture is suggested to be a result of the activated continental alkali–basaltic volcanism (Ishiga *et al.*, 1996). In opinion of cited authors, the inference is supported by high Zr and Hf concentrations in the studied deposits. The high content of P_2O_5 and Y is given similar explanation, because their concentrations in the continental basalts are much higher than those in MORB and tholeiites of oceanic islands (Ishiga *et al.*, 1996). The above characteristics indicate a more intensive transportation of continental material into the ocean. However, it should be noted that the high P_2O_5

content in the Lower Triassic sediments can have another cause, i.e., a significant influx of organic material.

There are two possible explanations of this phenomenon. The increased continental supply in the Early Triassic World Ocean may result either from the intensified geological activity, or from the sea transgression and more intense river runoff. A valuable indicator of these phenomena is the Ce content relative to other REE. As compared to the Pacific, the modern Atlantic Ocean is known to be characterized by higher Ce concentration that is caused by more active inflow of Ce-rich river waters (Musashino, 1990). In addition, the deep water masses are depleted in Ce relative to the surface water layer (Liu *et al.*, 1988). In the Sasayama and Tenjinmaru sections, the high Ce content is recorded in the Upper Permian deposits; it abruptly decreases in the Lower Triassic beds and gradually grows upward. This observation contradicts the assumption that the continental runoff into the Paleo-Pacific was intense. The assumption is also inconsistent with data on strontium isotope composition in carbonate sediments. In the Upper Permian deposits, the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios rapidly lower down to the minimum (0.7070) near the Permian–Triassic boundary (Smalley *et al.*, 1994). This trend suggests the increasing proportion of mantle influx into the World Ocean.

Different models are suggested to explain all geochemical phenomena observed and to settle the contradictions. According to one of them (Ishiga *et al.*, 1996; Kakuwa, 1996), the tectonic activity in the Permian–Triassic transition time improved connections between the Tethys and Paleo-Pacific. The water mass mixing caused a sudden change in the previously passive and stable Paleo-Pacific hydrodynamics that resulted in an active upwelling of bottom water masses depleted in Ce and O, but enriched in biologically active matter and toxic elements (Kakuwa, 1996a, 1996b). This induced the crisis of marine biological systems, which is manifested in the increased primary productivity of lower phytoplankton and in degradation of other groups. It should be noted that this model does not take into account the problem of water mass balance, because the water masses of the Paleo-Pacific were much more voluminous than those of the Tethys. Moreover, the destruction of oceanic barriers occurred more than once during the Phanerozoic history, but never resulted in rearrangement of the oceanic water structure.

Similar explanation is suggested for the behavior of sulfur isotopic ratios in the Motegi section of central Japan (Kamata and Kajiwara, 1996). Based on high $\delta^{34}\text{S}$ values (from -6 to -8.5%), the appearance of anoxic conditions during the Late Permian was suggested. Across the Permian–Triassic boundary, the $\delta^{34}\text{S}$ values abruptly decrease (down to -30%), and, in opinion of cited authors, this evidences a short-term cessation of anoxic conditions in response to the intensive

mixing of bottom and surface water masses. Afterward, in the earliest Triassic, the new phase of anoxic conditions gradually increased $\delta^{34}\text{S}$ values up to -10% and lasted for a long period, till the early Middle Triassic. The long-term anoxic event in the Early Triassic may be a consequence of events that activated oceanic hydrodynamics in the Permian–Triassic boundary time (Kamata and Kajiwara, 1996). The primary reason of hydrodynamic changes is unclear in this model.

According to another model, the eustatic fluctuations are factors responsible for typical anoxic events of the Mesozoic time. The model was discussed in detail by Gavrillov and Kopaeich (1996), who considered the Cenomanian–Turonian event as the principal example. In the Crimean sections, the anoxia-related deposits are enriched in organic carbon and toxic metals, such as Ni, Mo, and Zn. In general, a high content of toxic elements is characteristic of different deposits formed under anoxic conditions (Yudovich and Ketris, 1991). The organic carbon rapidly accumulated owing to the high primary productivity of phytoplankton and significant inflow of organic matter, nitrogen, and phosphorus compounds from continents. This was a response to the rapid flooding of vast maritime plains originated during the preceding regression. The concentration of toxic elements in sediments was favored by the lowered oxidation potential and by absorption of elements in sheaths of dead algae.

The comparison of these two models clearly shows the principal difference between anoxic events confined to the Permian–Triassic boundary and other Mesozoic epochs. In the first case, anoxia was caused by the upwelling of oxygen-deficient water masses rather than by transgression and subsequent phytoplankton bloom. This can explain the fact that the carbonaceous shales, which were formed under anoxic conditions, occur above the Permian–Triassic boundary in the Paleo-Pacific sections (Ishiga *et al.*, 1996; Kamata and Kajiwara, 1996). In this case, the active development of phytoplankton in pelagic settings of the Paleo-Pacific began after the mass extinction event and was for a long time a factor that decelerated restoration of marine biological systems. Therefore the mass extinction at the Permian–Triassic boundary was of a much greater significance than the biotic changes of the early Toarcian or Cenomanian–Turonian times.

Nevertheless, all the models suggested are disputable, and there are no sufficient data to prefer one of them. The most obscure are primary causes of the described events, and this aspect of the problem should be investigated further.

CONCLUSIONS

In the Paleo-Pacific deep-water sections, the Permian–Triassic boundary interval is characterized by significant changes in the taxonomic composition of fossil assemblages, and in lithology and geochemistry

of sediments. All these changes are directly connected with the most significant crisis in the biosphere that occurred near this boundary. Some changes are related to the causes of the crises, while others are its manifestations or consequences.

The negative Ce anomaly and positive anomalies of TiO_2 , P_2O_5 , and Y seem to be a consequence of the activate tectonic regime. This factor could provoke the biotic crisis.

The biotic crisis is manifested directly or indirectly in the sections studied. The direct manifestations are the extremely poor taxonomic composition of radiolarian assemblages and siliceous sponges. The indirect manifestations or consequences are the decreased rate of biogenic silica accumulation and widespread deposition of sediments enriched in organic matter.

The biotic and geochemical changes recorded in the sections are well correlative to each other and traceable in lateral directions (Figs. 1 and 2). On one hand, this suggests a connection between the biotic and abiotic phenomena, and, on the other, it is clear the integrated application of paleontological and geochemical data is useful for the stratigraphic scale refinement.

The large scale and duration of the Early Triassic crisis, along with its biotic, lithological and geochemical manifestations reveal its unique character in the history of the Earth and principal difference from other well known anoxic events.

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