

**$\delta^{13}\text{C}$  AND  $\delta^{18}\text{O}$  IN THE MAJOR PHANEROZOIC BOUNDARIES  
AND A MAIN REASON FOR A GREAT EXTINCTION**

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The reason for a great extinction of organisms at the P-Tr and K-P boundaries often attracts the investigator's attention. Within the Permian the anomalously high  $\delta^{13}\text{C}$  values are known in the Zechstein Formation of Germany (Kupferschiefer) and England (Marl Slate) (Magaritz and Turner, 1982), *Bellerophon* Formation of the Alps (Holser, 1994; Holser et al., 1989; Magaritz et al., 1988; Magaritz and Holser, 1991), Wargal (member 4b) and Lower Chhidru (member 2) Formations of Salt Range (Baud et al., 1995) and the Upper Capitanian - Lower Dzhulfian (Claystone III, Basal limestone, Anhydrite) (Glenister et al., 1992; Magaritz et al., 1983) of Texas.

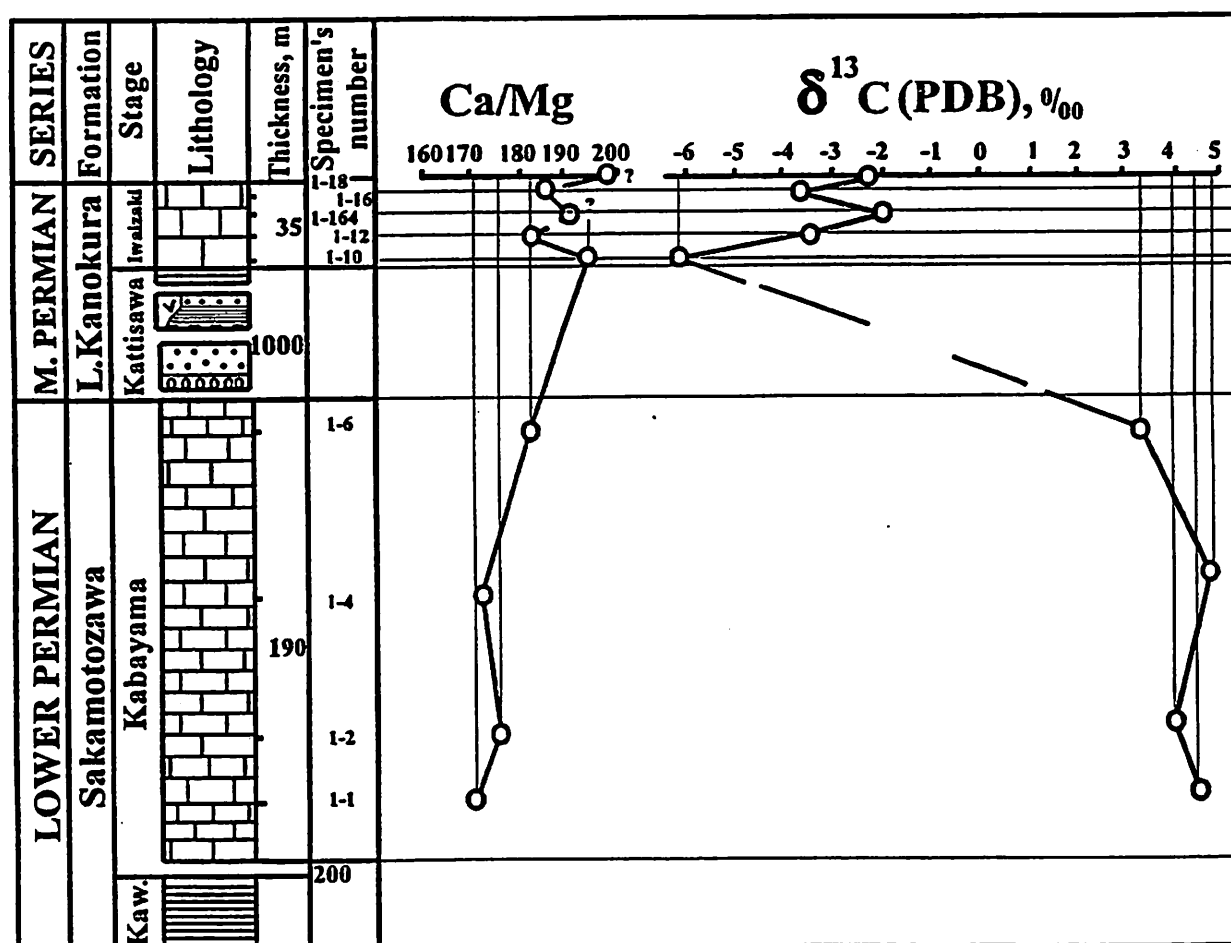


Fig. 1:  $\delta^{13}\text{C}$  and Ca/Mg ratio in black (Kabayama) and predominantly grey (Iwaizaki) limestones of the Lower and Middle Permian of Kannkurasawa-Kattisawa Valley region in Kitakami, Japan (Zakharov et al., in prep).

Positive shifts of  $\delta^{13}\text{C}$  were recently discovered in the Lower Permian black limestone (Sakamotozawa Series, Kawaguchi Stage) (3.9 - 4.7 ‰) (fig. 1) and upper Middle Permian limestone (Kanokura Formation, *Lepidolina multiseptata* zone, uppermost part of the member "f") (3.9 ‰) in Kitakami, Japan (Zakharov et al., in prep.), in the Midian - Dzhulfian boundary beds in the Transcaucasia (4.0 ‰) (fig. 2) and South Primorye (3.6 - 4.1 ‰) (fig. 3) (Zakharov et al., 1996a), characterized by a high index  $\delta^{13}\text{C}$  (Zakharov et al., in prep.).

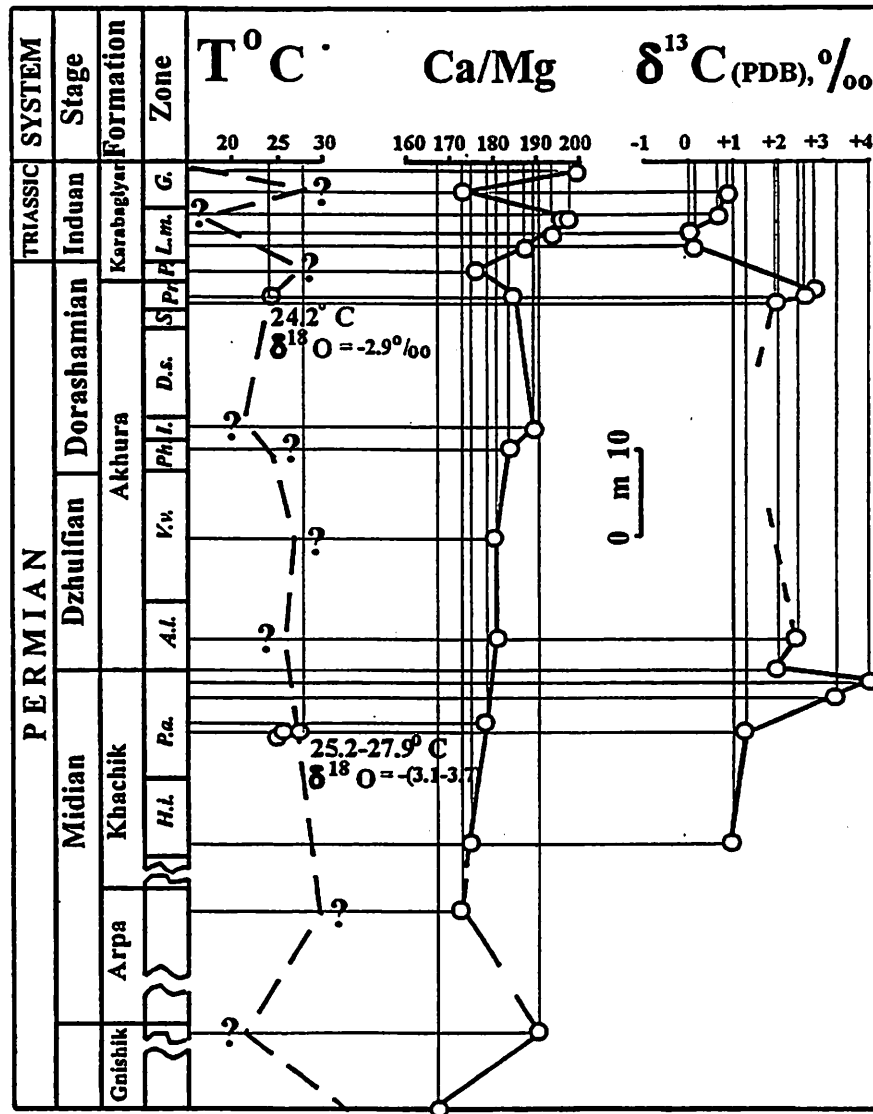


Fig. 2: Paleotemperature and positive shift of carbon isotopes in Transcaucasia during the Permo-Triassic. \*Paleotemperature fluctuation tendency is shown on the basis of data on  $\delta^{18}\text{O}$  and Ca/Mg ratio (Zakharov et al., 1996a). Abbreviated name of Zones: H.i. = Hemigordius irregulariformis - Orthotetina azarjani, P.a. = Pseudodunbarula arpaensis - Araxilevis intermedius, A.l. = Araxoceras latissimum, V.v. = Vedioceras ventrosulcatum, Ph. = Phisonites triangulus, I = Iranites transcaucasicus, D.s. = Dzhulfites spinosus, S. = Shevyrevites shevyrevi, Pr. = Paratirolites kittli, P. = Pleuronodoceras occidentale, L.m. = Lytophicerus medium, G. = Gyronites.

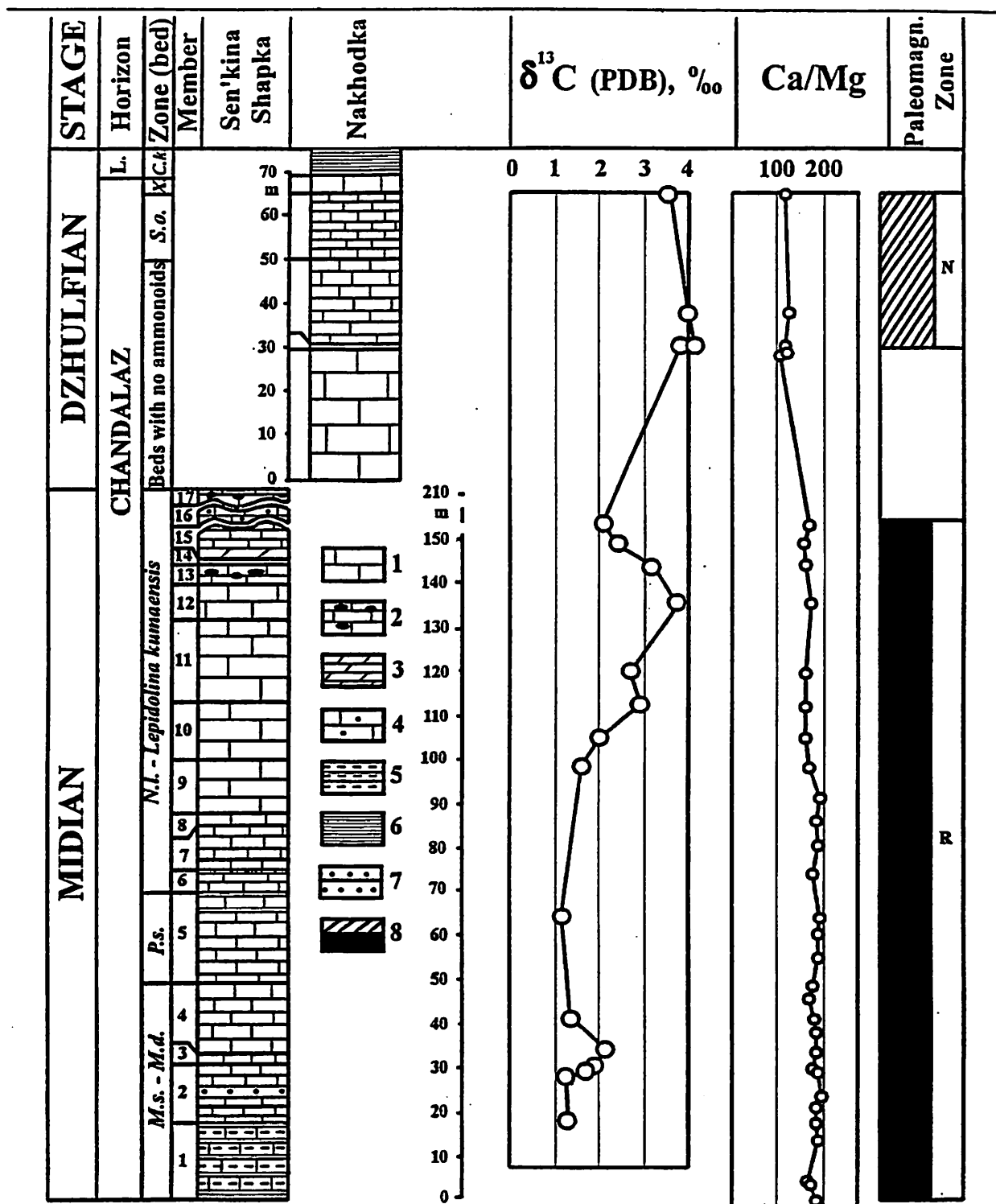


Fig. 3:  $\delta^{13}C$  and Ca/Mg ratio fluctuations in limestones of the Upper Midian- Lower Dzhulfian interval (Upper Permian) in South Primorye (Zakharov et al., 1996a). Abbreviated name of Zones (Beds, Horizon): Ms. - M.d. = *Monodioxodina sutschanica* - *Neomisellina dutkevitchi*, P.s. = *Parafusulina stricta*, N.l. = *Neomisellina lepida* - *Lepidolina kumaensis*, S.o. = *Stacheoceras orientale*, X = *Xenodiscus subcarbonarius*, C.k. = *Cyclolobus kiselevae*, L. = *Lyudyanza* Horizon.

Another significant event of the Late Paleozoic - Early Mesozoic is a sharp decrease of  $\delta^{13}\text{C}$  in the sediments of the Permian and Triassic boundary beds. A short-term fall of temperature at the beginning of the Induan stage soon followed by a warm period (recognized somewhat conditionally from Ca/Mg of carbonates of the *Lytophiceras medium* zone in Transcaucasia) corresponds, apparently, to the time of the Siberian trap injection.

$\delta^{13}\text{C}$  (PDB), ‰

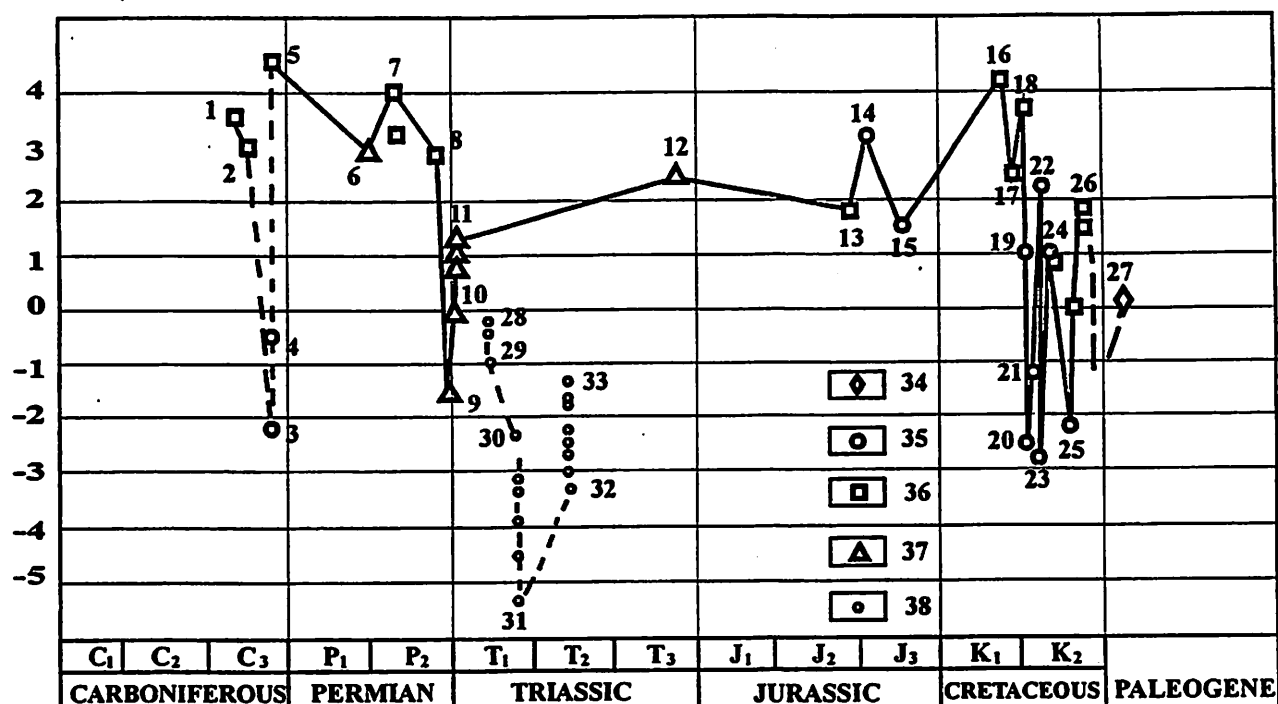


Fig. 4:  $\delta^{13}\text{C}$  fluctuations during the Late Paleozoic and Mesozoic. 1-27 - carbonates of the Tethys, 28-32 and, apparently, 3-4 - carbonates of the Boreal realm: 1 - Missurian of Texas (Grossman et al., 1991), 2 - lower Virgilian of Texas (Grossman et al., 1991), 3-4 - Gzhelian of Urals, 5 - upper Virgilian of Texas (Grossman et al., 1991), 6 - Kubergandinian of Crimea, 7 - Midian-Dzhulfian boundary beds of Transcaucasia, 8 - Dorashamian of Transcaucasia, 9 - lower Induan of South China, 10 - lower Induan (the base of the Ophiceras (*Lytophiceras*) medium beds) of Transcaucasia, 11 - upper Ophiceras (*Lytophiceras*) medium beds of Transcaucasia, 12 - Norian of Crimea, 13 - Upper Callovian of Oka River basin, 14 - Oxfordian of England (Anderson et al., 1994), 15 - Kimmeridgian-Tithonian of West Mediterranean (Price and Sellwood, 1994), 16 - Aptian of the southern Alps (Erbacher, 1994; Coccioni, 1996), 17 - Albian of the southern Alps and England (Erbacher, 1994; Gale, 1995; Jenkyns et al., 1994; Coccioni, 1996), 18 - Cenomanian-Turonian boundary beds of the southern Alps and England (Erbacher, 1994; Gale, 1995; Jenkyns et al., 1994; Coccioni, 1996), 19 - Upper Turonian of Hokkaido, 20 - Turonian of Koryak Uplands, 21 - Coniacian of Hokkaido, 22 - Upper Santonian of Hokkaido, 23 - Lower Campanian of Sakhalin, 24 - Upper Campanian of Sakhalin, 25 - Lower Maastrichtian of Sakhalin, 26 - middle Upper Maastrichtian of Sakhalin, 27 - middle Danian (middle Sinegorsk member) of Sakhalin, 28 and 29 - Lower Olenekian of Buur River basin in Arctic Siberia, 30 and 31 - Upper Olenekian of Olenek River (Mengilyakh Creek), 32 and 33 - Upper Anisian of Taimir, 34 - bivalve shells of lower paleolatitudes, 35 - cephalopod shells of lower paleolatitudes, 36 - brachiopod shells of lower paleolatitudes, 37 - limestones of lower paleolatitudes, 38 - ammonoid shells of high paleolatitudes.

There are grounds to consider that the low index of  $\delta^{18}\text{O}$  in the aragonitic cephalopod shells from the Lower Olenekian (Buur River), Upper Olenekian (Olenek River, Mengilyakh) and Anisian (Taimir) of Arctic Siberia was caused by the recurrent fresh-water influence at that part of the Boreal realm (Zakharov, Ukhaneva, Ignatyev et al., in press).

A relatively high index of  $\delta^{13}\text{C}$  was found in carbonates of the middle Mesozoic: Norian of Alma River in Crimea (2.4 ‰) (Zakharov, Ukhaneva, Ignatyev et al., in press), Oxfordian of England (Anderson et al., 1994), Aptian (Erbacher, 1994) and Cenomanian-Turonian boundary beds (Erbacher, 1994; Gale, 1995; Jenkyns et al., 1994; Coccioni, 1996) of the southern Alps and England (fig. 4).

Data on Late Turonian, Coniacian and Santonian  $\delta^{18}\text{O}$  have not yet been reported from Sakhalin, but new information on Japan (Zakharov et al., in prep.) confirm the existence of a climatic optimum (14.1-19.6 °C in Hokkaido) and a zone of relatively high  $\delta^{13}\text{C}$  values (2.5‰ in Hokkaido) during the Santonian (fig. 5).

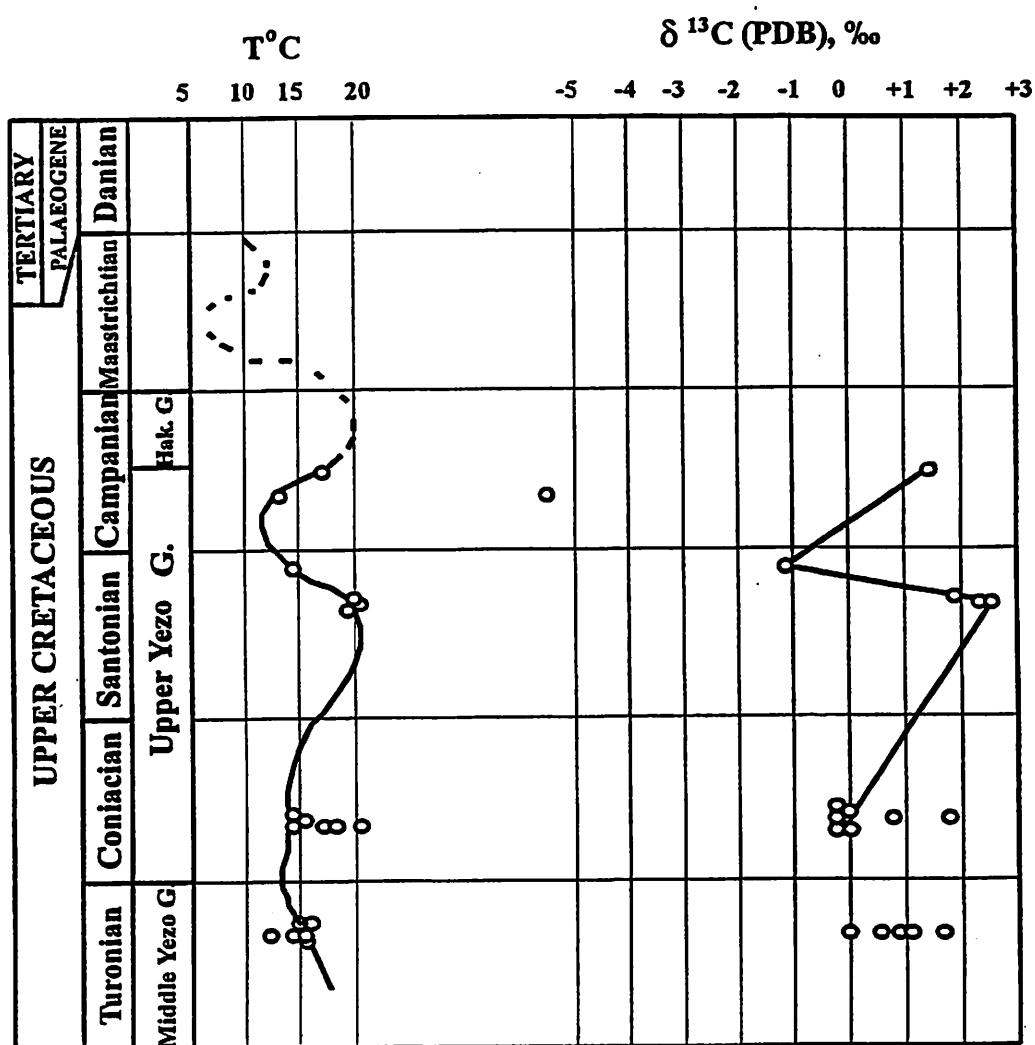


Fig. 5: Paleotemperature and positive shifts of carbon isotopes in Hokkaido during the late Cretaceous (Zakharov et al., in prep.). Hak. = Hakubachi Group.

The Late-Middle Campanian is characterized by positive shifts of  $\delta^{13}\text{C}$  (1.4‰ in Hokkaido and 1.0‰ in Sakhalin), negative  $\delta^{18}\text{O}$  excursion (climatic optimum with temperature about 18 °C in Sakhalin), sea-level regression, rapid polarity changes and the beginning of the strong volcanic activity (fig. 6). During Early Maastrichtian, a drop in temperature (5.2 °C in Sakhalin) happened;  $\delta^{13}\text{C}$  data (-2.5‰ in Sakhalin) suggests that there was a sharp drop in organic productivity. The  $\delta^{13}\text{C}$  index of middle Late Maastrichtian carbonate is relatively high (1.4 - 1.8‰ in Sakhalin). A sharp fall of temperature in the Maastrichtian - Danian boundary time is expected just after some warming (about 10-11 °C in Sakhalin) during the middle Late Maastrichtian (Zakharov et al., 1996b).

It seems justified to assume that the repeated influence of the three basic factors: drop of temperature, oxygen deficit and enormous eustatic level fluctuation (figs. 6, 7), provoked by thermal perturbation at the core/mantle boundary and change in rotation regime of the Earth (speed of Earth rotation) (Krassilov, 1985; Zakharov, 1986; Canaghan et al., 1994) is the main reason for the destruction of epicontinental sea ecosystems both at the end of the Permian and the end of the Cretaceous.

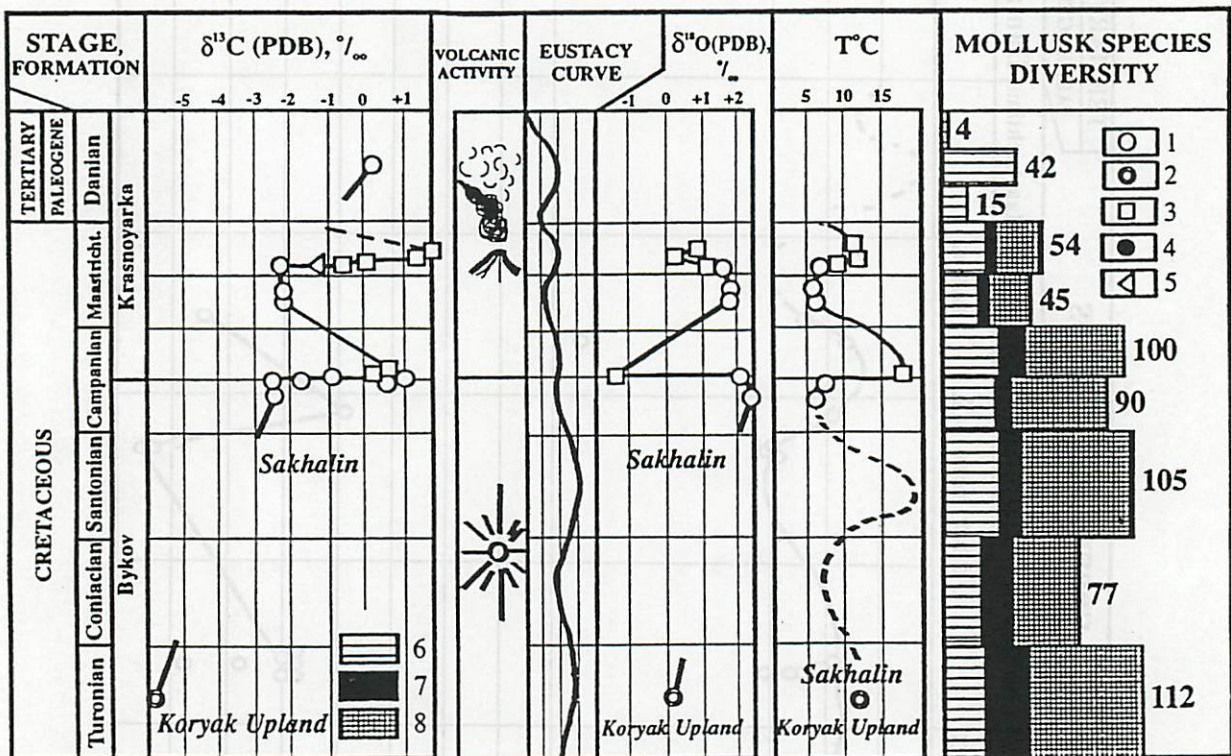


Fig. 6: Correlation of isotopic/chemical shifts, volcanic activity intervals, main changes in climate and mass extinction in South Sakhalin and adjacent territory during late Cretaceous - early Tertiary. 1 - ammonoids from South Sakhalin, 4 - bivalves from South Sakhalin, 5 - sedimentary rock from South Sakhalin, 6 - non-inoceramid bivalve species, 7 - inoceramid bivalve species, 8 - ammonoid species.

GEOLOGICAL TIME SCALE (with magnetic polarity data)	FORMATION	BEDS	PHASE	BIOEVENT	AMMONOID SUCCESSION			T°C	TERRESTRIAL (SEASHORE) PLANT TYPE	BASIC FACTORS OF SYNGENESIS			
					DOMINANT	Quantity (genera, species)	N						
TERTIARY UPPER CRETACEOUS	Krasnoyarsk	6	6	-	Rare specimens	0	0	0	-	Destruction of the marine communities as a result of shoaling and bogging. Homeostatic development under influence of increase of warmth. Destruction of marine communities as a result of temperature fall during early Maastrichtian and Cretaceous-Tertiary boundary time (because of next portions of volcanic activity) and, apparently, fluctuating anoxic conditions.			
					Thyasira uncinata	0	0	0	-		Mixed coniferous (Metasequoia)-platanophyllous forest		
					Pseudaphrodina extrema	0	0	0	-				
					Pachydiscus subcompressus-P.b.	17	26	N	6.0-9.3	Mixed coniferous (Sequoia)-?platanophyllous forest			
					Zelandites japonicus	19	23	1.2N	5.3				
					Canadoceras kossmati	(18)	(23)	10N	18.1	Fern-laurophyllous Ginkgo forest			
		Anapachydiscus naumanni-Peron.	28	54		5.4-5.9							
		LOWER CRETACEOUS	Naiba	1	1	-	Rare specimens	5	7	0.3N	-	Homeostatic development under existing conditions of the comparatively fluctuating climate (with maximum of temperature fall during Cretaceous and middle Campanian), but normal salinity conditions. The middle Campanian temperature fall is connected with the beginning of volcanic activity, which followed the rise of the unstable palaeomagnetic field. The increase of warmth in late Campanian was probably provoked by the hotbed effect of atmosphere as a result of the increase of carbonic acid concentration of volcanic origin. Destruction of the marine communities as a result of the recurrent fresh-water influence.	
							Jimboiceras mihouense	(16)	(28)				Mixed coniferous-platanophyllous fern forest
							Jimboiceras planulatifforme	22	39	15N	11.7		
Marshallites Acanthoceras san.	(13)						(16)			Mixed coniferous-Ginkgo forest			
Turritites costatus	30	6	7N		Predominantly fern forest								
Cleoniceras	(3)	(3)				Ginkgo and fern forest							

Fig. 7: Faunal and floral succession during the Cretaceous and early Tertiary in South Sakhalin. Normal magnetic polarity is indicated by black colour (Geological Time Scale, 1983). Data in brackets indicate the number of species in common. N = ammonoid abundance during Late Maastrichtian (to make a comparison with Albian-Danian time).

## References

- ANDERSON, T.F., POPP, B.N., WILLIAMS, A.C., HO, L.-Z. and HUDSON, J.D., 1994. The stable isotopic records of fossils from the Peterborough Member, Oxford Clay Formation (Jurassic), U.K.: palaeoenvironmental implications. *J. Geol. Soc., London*, 151: 125-138.
- BAUD, A., ATUDOREI, V. and SHARP, Z., 1995. The Upper Permian of Salt Range area revisited: new stable isotope data. *Permophiles*, 27: 39-41.
- CANAGHAN, P.J., SHAW, S.E. and VEEVERS, J.J., 1994. Sedimentary evidence of the Permian/Triassic global crisis induced by the Siberian hotspot. *Can. Soc. Petrol. Geol., Mem.*, 17: 785-795.
- COCCIONI, R., 1996. The Cretaceous of the Umbria-Marche Apennines (Central Italy). *Cretaceous stratigraphy, paleobiology and paleobiogeography. J. Wiedmann Symposium. Abstracts*, Tübingen: 129-136.
- ERBACHER, J., 1994. Entwicklung und Paläoozeanographie mittelkretazischer Radiolarien der westlichen Tethys (Italien) und des Nordatlantiks. *Tübinger Mikropalaeont. Mitt.*, 12: 1-139.
- GALE, A.S., 1995. Cyclostratigraphy and correlation of the Cenomanian Stage in Western Europe. *Orbital Forcing Timescales and Cyclostratigraphy. Geol. Soc. Spec. Publication*, 85: 177-197.
- GEOLOGICAL TIME SCALE, 1983. *Geol. Soc. America, Boulder*, pp. 1-2.
- GLENISTER, B.F., BOYD, D.W., FURNISH, W.M. et al., 1992. The Guadalupian: proposed international standard for a Middle Permian series. *Intern. Geol. Review*, 34(9):857-888.
- GROSSMAN, E.L. and KU, T.-L., 1986. Oxygen and carbon isotope fractionation in biogenic aragonite: Temperature effect. *Chem. Geology*, 59: 59-74.
- GROSSMAN, E.L., ZHANG, C. and YANCEY, T.E., 1991. Stable-isotope stratigraphy of brachiopods from Pennsylvanian shales in Texas. *Geol. Soc. Amer. Bull.*, 103(7): 953-965.
- HOLSER, W.T., 1994. Gradual and abrupt shifts in ocean chemistry during Phanerozoic time. *Patterns of Change in Earth Evolution. Springer Verlag, Berlin, Heidelberg, New York, Tokyo*, pp. 123-143.
- HOLSER, W.T., SCHONLAUB, H.P., ATTREP, M. et al., 1989. A unique geochemical record at the Permian-Triassic boundary. *Nature*, 337(6202): 39-44.
- JENKYN, H.C., GALE, A.S. and CORFIELD, R.M., 1994. Carbon- and oxygen-isotope stratigraphy of the English Chalk and Italian Scaglia and its palaeoclimatic significance. *Geol. Magazine*, 131: 1-34.
- KRASSILOV, V.A., 1985. Cretaceous evolution of the Earth-crust and biosphere. *Nauka, Moskva*: 1-240 (in Russian).
- MAGARITZ, M., ANDERSON, R.Y., HOLSER, W.T. et al., 1983. Isotope shifts in the Late Permian of the Delaware Basin, Texas, precisely timed by varved sediments. *Earth and Planetary Sci. Letters*, 66: 111-124.
- MAGARITZ, M., BAR, R., BAUD, A. and HOLSER, W.T., 1988. The carbon-isotope shift at the Permian/Triassic boundary in the southern Alps is gradual. *Nature*, 331(6154): 337-339.
- MAGARITZ, M. and HOLSER, W.T., 1991. The Permian-Triassic of the Gartnerkofel-1 core (Carnic Alps, Austria): carbon and oxygen isotope variation. *Abhandl. geol. Bundesanstalt*, 45: 149-163.
- MAGARITZ, M. and TURNER, P., 1982. Carbon cycle changes of the Zechstein Sea: isotopic transition zone in the Marl Slate. *Nature*, 297(5865): 389-390.
- PRICE, G.D. and SELLWOOD, B.W., 1994. Palaeotemperature indicated by Upper Jurassic (Kimmeridgian-Tithonian) fossils from Malorca determined by oxygen isotope composition. *Palaeogeogr., Palaeoclimatol., Palaeoecol.*, 110: 1-10.
- ZAKHAROV, Y.D., 1986. Macroevolution and the major boundaries in the Phanerozoic. *Eclog. geol. Helv.*, 79: 227-235.
- ZAKHAROV, Y.D., IGNATYEV, A.V., KOTLYAR, G.V., UKHANEVA, N.G., and CHERBADZHY, A.K., 1996a. Permian-Triassic stable carbon isotopes and Ca-Mg carbonate relations and mass extinction. *Tikhookeanskaya geologiya*, 15(1): 3-15 (in Russian).
- ZAKHAROV, Y.D., IGNATYEV, A.V., UKHANEVA, N.G., and AFANASEVA, T.B., 1996b. Cretaceous ammonoid succession in the Far East (South Sakhalin) and the basic factors of syngeneses. *Bull. Inst. royal Sci. nat. Belgique, Sciences de la Terre*, 66: 109-127.
- ZAKHAROV, Y.D., UKHANEVA, N.G., IGNATYEV, A.V., AFANASEVA, T.B., VAVILOV, M.N., KOTLYAR, G.V., POPOV, A.V. and POPOV, A.M., (in press). New data on  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in Paleozoic and Mesozoic organogenic carbonates of Eurasia and the problem of salinity in the Boreal basin in the beginning of Mesozoic. *Tikhookeanskaya geologiya* (in Russian).