Stable Carbon Isotopes and Ca/Mg Ratio in the Permo-Triassic Carbonates and Mass Extinction of Organisms

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Data on the carbon-isotopic composition of the Upper Permian and the lowermost Induan Stage carbonates allow the recognition of two major environmental changes that made a significant impact on the evolution of the biosphere. The late Capitanian–Djulfian event, recognized by abnormally high δ^{13} C values (up to 4.1–7.5‰) in Eurasian (Zechstein, Alpine province, South Primorie, and Spitsbergen?) and North American (Texan) carbonates is explained by an unusually high C_{org} content in the ocean of that time, probably due to the high productivity of the biota existing in the mostly warm, humid climate. An abrupt decline in the heavy-carbon isotope concentration at the base of the Induan Stage, accompanied by a considerable decline in the Mg content in the carbonates of the Tethyan province might have been induced by a dramatic decline in the photosynthesis on the continents, under the influence of a cold, arid climate and a considerable decrease in the biological productivity of the seas in response to marine regression and an increasing deficiency in oxygen. It is safe to suggest that the main reason for the assumed short-term cooling of climate corresponding with a δ^{13} C zonal moment in the Induan Stage and followed by a warming event, were the volcanic processes that took place between the Permian and Triassic.

INTRODUCTION

Recently, much of the literature has been published on studies of the isotopic composition of the Paleozoic and Mesozoic-Cenozoic biogenic carbonates and reconstructions of the habitat of the fossil organisms living there. Most interesting, in our opinion, are the investigations that indicate dramatic changes in the carbon-isotopic composition at the principal Phanerozoic chronostratigraphic boundaries, and the isotopic anomalies that occurred just before these events [15], [17], [20], [25], [27], [28], [29], [30], [31], [32], [37], [38], [39], [40], [41], [42], [44], [46], [47], [48].

This paper presents new data on the carbon-isotopic anomaly discovered in the Permian of South Primorie and data on Ca-Mg ratio values of the Upper Permian and the lowermost Triassic carbonates (taking account of the isotopic data) with reference to key sections in Trans-Caucasia, Primorie, and South China.

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SOUTH PRIMORIE

The Permian carbonate strata in South Primorie are most fully represented in the Partizanskaya River basin and near Nakhodka. The bulk of the limestones are confined to the Chandalaz Horizon of the Upper Permian, where the sequence contains three fusulinid zones and several fossiliferous beds [6], [10], [33]. The Permian sequence in South Primorie is overlain by the Lyudyanzin Horizon, composed of mostly clastic deposits. Geochemical and physical investigations included only the Upper Permian rocks of the Chandalaz Horizon (according to the original interpretation of [13], the Nakhodka reef limestones belong to the upper part of that horizon).

Senkina Shapka Mountain

The stratotype of the three fusulinid zones encompassing the main part of the Chandalaz Horizon is the Mt. Senkina Shapka section [7], [10], [33]. This is located on the right bank of the Partizanskaya River, 2.5 km southwest of the Lozovaya railway station.

The lithology and fossil data for its major units are given below (upward); hereafter the sampling sites are indicated in parentheses:

1. Monodiexodina sutschanica-Metadoliolina dutkevichi Zone.

Limestones, silty and sandy limestones (851-1 - at the bottom of the zone, 851-3 - 8.9 m; 851-5 - 12.9 m; 851-7 - 15.98 m; 851.8 - 17.9 m; 851-10 - 19.9 m; 851-11 - 20.8 m; 851-13 - 24.4 m; 851-15 - 28.6 m; 851.17 - 32.1 m; 851.19 - 35.8 m and more above the base of the zone, 851-21 - at the top of the zone) [7]. Thickness 40 m.

Foraminifera: Sichotenella, Reichelina, Monodiexodina, Neomisellina, Pachyphloia, Cylindrocolaniella, Minojapanella, Chusenella, Pseudofusulina, Parafusulina, and Arenovidalina [10], [33].

Bryozoans: Dyscritella, Coscinotrypa, and Fistulipora [33].

Brachiopods: Debrya grandis Waag., Linoproductus ex gr. lineatus Waag., Waagenoconcha cf. keilhavi (Buch.) [10], [33].

Conodonts: Hindeodus minutus Ellis (identified by S. V. Rybalka [33]).

2. Parafusulina stricta Zone.

Limestones with thin mudstone interbeds (851-23 - 4.0 m, 851-25 - 12.0 m, 851-27 - 18.2 m above the base of the zone). Thickness 21 m.

Foraminifera: Sichotenella, Rauserella, Kahlerina, Pseudokahlerina, Parareichelina, Minojapanella, Codonofusiella, Lantchichites, Parafusulina, Pseudofusulina, Lepidolina, Pseudoliolina, Agathamina, Langella, Pachyphloia, and Cylindrocolaniella [10], [33].

Bryozoans: Dycritella, Fistulipora, Eridopora, Fistulamina, Epiactinotrypa, Streblascora, Primorella, Fenestella, Septopora, Polypora, and Girtyporina [33].

Brachiopods: Tyloplecta yantseensis Chao, Leptodus richtofeni Keys., L. nobilis (Waag.), Haydenella kiangsiensis (Keys.), Cleiothyridina accola (Reed), Gefonia plicata Lich., Notothyris nucleolus Kut., and Rostranteris cf. ovale (Gemm.) [10], [33].

3. Neomisellina lepida-Lepidolina kumaensis Zone.

Limestones with thin mudstone and marl interlayers and siliceous limestone nodules (851-30 - 4.7 m, 851-32 - 9.8 m; 851-34 - 16.6 m, 851-36 - 22.1 m, 851-38 - 28.8 m, 851-40 - 35.7 m, 851-43 - 44.9 m, 851-045 - 52.6 m, 851-47 - 58.2 m, 851-49 -63.9 m, 851-51 - 69.0 m, 851-53 - 76.7 m, 851-55 - 82.3 m, 851-57 - 87.2 m above the base of the zone). Thickness 144 m.

Foraminifera: Sichotenella, Kahlerina, Pseudikahlerina, Neomisellina, Lantchichites, Pseudofusulina, Lepidolina, Reichelina, Parareichelina, Rauserella, Pseudodoliolina, Yabeina, Codonofusiella, Minojapanella, Bradyina, Robuloides, Partizania, Pseudowanganella, Pachyphloia, Dagmarita, and Abadehella [10], [33].

Bryozoans: Fistulipora, Parastenodiscus, and Girtypora [33].

Corals: Wentzelella orientalis Ivan., Polythecalis flatus Huang, P. chandalasiense Krop., W. kueichowense Huang, Polythecalis yangtzeensis hochovensis Font., and P. pulchrum Krop [33].

Brachiopods: Rhipidomella cf. vediensis Sok., Bathymyonia barabaschensis Kotl., Haydenella tumida Waag., H. kiangsiensis Masl., Cleiothyridina maynci Dunb., Hemiptychina himalayensis Dav., Transennatia gratiosa (Waag.), Tyloplecta yangtzeensis Chao, Phricodothyris asiatica Chao, and Husatedia gradicosta (Dav.) [33].

Nakhodka Reef

It is generally agreed [6], [9], [10], [33] that the limestones of the Nakhodka reef located

near the oil store (an old quarry) of the town of Nakhodka some 35.5 km southwest of Mt. Senkina Shapka, are an extension of the Permian sequence of that mountain.

The following beds are recognized here (upward):

1. Beds without ammonoids. Gray biogenic limestones (854-4, 4a, 4b - 31-41 m; 854-3 - 39-49 m above the base of the member). Thickness 54-67 m.

Bryozoans were recognized in a fragment from the talus.

2. Beds with *Stacheoceras orientale*. Reefal limestones, gray, brecciated, crinoidbearing. Thickness 10-17 m.

Foraminifera: Genitzinita, Robuloides, Tuberitina, Neoendothyra, Nodosaria, Lasiodiscus, and Arpella [9], [10], [33].

Bryozoans: Fistulipora, Stenodiscus, Streblascopora, Rectifenestella, and Girtyporina [33].

Corals: Paracaninia subtilis (Nierman), Polycelia sp., and Lophocarinophyllum sp. [9], [10].

Sphinctozoans: Taumastocoelia sp., Solassia arta Bel., Henricellum sp. I, Celyphia permica Bel., Follicatena callosa Bel., Ambysiphonella asiatica Ju, A. yini Zhang, A. obliquisepta Zhang, Intrasporeocdoelia orientalis Bel., I. robusta Bel., Rhabdactinia columnaria Yabe et Sug., Cystotalamia crassa Bel., C. aff. nudulifera Girti, and Polycystocoelia cf. huajiapengensis Zang [33].

Crinoids: Araxicrinus aff. papillaris Stuck [22].

Brachiopods: Edriosteges poyangensis (Keys.), Strofalociina tibetica (Dien.), Leptodus nobilis (Waag.), Squamularia grandis Chao, Chenxianoproductus nachodkensis Kotl., Lamnimargus himalayensis (Dien.), Anidantus sinosus Huang, Stenoscisma margaritovi (Huang) [9], [10], [33].

Cephalopods: Pseudothoceras? sp., Eumedlicottia nikitinae Zakh., Neogeoceras thaumastum Ruzh., and Stacheoceras oriental Zakh. [6].

Outside the Nakhodka reef, the index species of the beds (*Stacheoceras orientale*) is found in calcareous nodules in the shale facies of the Tungus Bay [6].

3. Beds with *Xenodiscus subcarbonarius*. Reefal limestones, gray and dark-gray, brecciated, crinoid-bearing (854-1,2 from the basal layer). Thickness 3-4 m.

Small foraminifera: Lasiodiscus, Glomotrocholina, Agathammna, Robuloides, and Arpella [9], [10], [33].

Fusulinids: Codonofusiella, Reichelina, and Rauserella [33].

Bryozoans: Fistulipora, Stenodiscus, Streblascopora, Rectifenestella, and Girtyporina

[33]. In all probability, Rhabdomeson, Claussotrypa, and Pennireteropa (identified by

A.V. Kiseleva) also originate from these beds of the Nakhodka reef.

Corals: *Pseudofavosites kotljarae* Ivan. et Krop., and *Callophyllum kabakovitchae* Iljina [9], [10].

Sphinctozoans: Solassia arta Bel., Celyphia permica Bel., Follicatena callosa Bell., Apocoelia orientalis Bel., Colospongia nachodkiensis Bel., C. globosa Bel., Amblysiphonella asiatica Ju, A. eleganta Bel., A. yini Zhang, A. vesiculosa (Kon), A. obliquisepta Zang, Polysiphonella insolita Bel., Intrasporeocelia robusta Bel., I. orientalis Bel., Cystothalamia crassa Bell., Preverticilites columnella Parana [33].

Brachiopods: Peltichia nachodkensis Kotl., Strophalosiina tibetica (Dien.), Chenxianoproductus nachodkensis Kotl., Lamnimargus himalaensis (Dien.), Spinomarginifera grandis (Kotl.), Anidanthus sinosus (Huang), Caucasoproductus primoricus Kotl., Leptodus nobilis Waag., Choristitella wynnei (Waag.), and Squamularia grandis Chao [9], [10], [33].

Bivalves: Parallelodon, Myaolina, Aviculopecten, Acanthopecten, Streblochondria, Eocamptopecten, Cyrtorostra, Paleolima, and Edmondia [9].

Cephalopods: Neocycloceras? sp., Lopingoceras sp., Paratainonautilus sp., Permonautilus sp., Permorhynchus dentatus Zakh., Neogeoceras thaumastum Rruzh., and Xenodiscus subcarbonarius Zakh. [6].

Conodonts: *Sweetognatus* sp. nov. aff. *iranicus* Koz., *Gondolella* sp. (a poorly preserved fragment probably belonging to *G. orientalis* Bars. et Koz., identified by H. Kozur) [12].

Shales of the Lyudyanzin Horizon, overlying the limestones at this site, contain the remains of the Late Permian ammonoids - *Propinacoceras* sp. and *Cyclolobus* sp. (10 m above the base of the horizon).

The Nakhodka reef limestones are essentially different from the rocks of Mt. Senkina Shapka (except for the upper beds of the sequence) in their abundance of heavy-carbon and magnesium isotopes. Their δ^{13} C values reach 3.6-4.1‰, whereas in much of Mt. Senkina Shapka sequence (the lower part) they amount to just 1.4-2.2‰ (Table 1). No essential changes in the heavy-oxygen isotope abundances have been detected in the carbonate Permian sequence of South Primorie (Table 1). At the same time, the beds lying above the *Metadoliolina lepida-Lepidolina kumaensis* Zone show an abrupt increase in the magnesium abundance of the limestones (Table 2).

SOUTH CHINA

Given below in the description of the sequence are unique data on the samples collected during the excursion held by the International Conference on the Permo-Triassic (Beijing, September 1987).

Chongqing

The Permo-Triassic sequence in the Liangfeng district (Chongqing) [44] consists of the following units (upward):

Sample	Zone, beds	Locality	Member	δ ¹¹ C(PDB)	δ ^{1 *} O	δ ^{1 8} Ο
•		2000000		%•	(SMOW)‰	(POB) ‰
851-5	Monodiexodina sutchanica -	Senkina Shapka	1	+ 1.4	+20.7	-9.2
	Neomisellina dutkevichi					
851-9	_ •		2	+1.4	+22.1	-7.8
851-10	- •	- ·	2	+1.8	+21.9	-8.0
851-11	_ • -	- ·	3	+2.0	+22.4	-7.5
851-13	_ • _		4	+2.2	+22.3	-7.6
851-17	_ ·		4	+1.5	+22.6	-7.3
851-27	Parafusulina stricta		5	+1.3	+23.1	-6.2
851-38	Neomisellina lepida -		9	+1.7	+21.6	-7.7
	Lepidolina kumaensis]	1	ļ		
851-40			10	+2.1	+22.0	-7.3
851-43	- *		11	+3.0	+22.3	-7.0
851-45		- ·	11	+2.8	+21.3	-8.0
851-51			12	+3.8	+23.6	-5.7
851-53	↓ — • —	- •	13	+3.2	+21.1	-8.2
851-55	- · -		15	+2.5	+21.2	-8.1
851-57			15	+2.2	+21.7	-7.6
851-4	Beds without	Nakhodka	19	+3.9	+22.1	-7.8
854- 4ac	_ *		19	+4.1	+24.1	-5.8
854- 3			20	+4.0	+21.8	-8.1
854- 1	Xenodiscus subcarbonarius		22	+3.6	+20.5	-9.4
		L	1	I		

 Table 1
 Carbon and oxygen isotopic ratio in the limestones of the Chandalaz Horizon in South

 Primorie.
 Primorie.

Changxing Formation. 1. Marls, limestones, and mudstones. Thickness 8.6 m. Brachiopods: Oldhamina, Haydenella, and Uncinunellina.

2. Limestones, muddy limestones, calcareous shales (Sample N KT-17). Thickness 3.5 m.

Brachiopods: Oldhamina and Araxathyris.

3. Limestones, cherts, mudstones. Thickness 12 m.

Foraminifera: Palaeofusulina, Codonofusiella, Reichelina.

Brachiopods: Perigeyerella, Leptodus, Dielasma, Tschernyschewia, and Haydenella.

4. Marls, limestones, mudstones. Thickness 13.5 m.

Foraminifera: Palaeofusulina and Reichelina.

Brachiopods: Perigeyerella, Leptodus, Dielasma, Tschernyschewia, Haydenella, and Squamularia.

5. Limestones. Thickness 43.5 m.

Foraminifera: Palaeofusulina, Reichelina, and Colaniella.

Brachiopods: Enteletina, Meekella, Perigeyerella, Chonetinella, Waagenites, Leptodus, Neowellerella, and Araxathyris, etc.

6. Limestones, siliceous limestones, and shales. Thickness 6.3 m.

Sample	Zone, beds	Locality	Ca, %	Mg, %	Ca/Mg
1	2	3	4	5	6
851-1	Monodiexodina sutchanica -	Senkina Shapka	39.1029	0.19329	202.301
	Neomisellina dulkevichi		1		
851-2		l _ • _	38.489	0.2122	181.38
851-3		- "	39.496	0.194	203.566
851-5	_ · -		39.9877	0.1967	203.292
851-7	- • -		38.13	0.1879	202.927
851-8	- · -	- • -	38.4404	0.1831	209.942
851-10	"		38.1024	0.1924	198.037
851-11	_ · _	1 - • -	38.1473	0.1973	193.345
851-13	"		38.2042	0.1902	200.86
851-15	- · -	- · -	38.2424	0.19	201.275
851-17	_ · _	_ · _	38.486	0.2001	192.333
851-19		— · —	38.4791	0.221	174.9
851-21		- • -	38.506	0.1996	192.915
851-23	Parafusulina stricta		38.4421	0.188	204.479
851-25		_ • _	38.51	0.1909	201.729
851-27	_ · -	_ • _	38.448	0.19	202.357
851-30	Neomisellina lepida -		38.541	0.2042	188.741
	Lepidolina kumaensis	1 I			
851-32	- · -		38.44	• 0.19	202.315
851-34			38.5111	0.1913	201.312
851-36		- · -	39.4932	0.1941	203.468
851-38			37.66	0.21	179.35
851-40			37.86	0.219	172.2
851-43		- · -	37.4	0.22	169.5
851-45			37.58	0.22	170.55
851-51			37.38	0.208	179.55
851-53			37.59	0.218	172.35
851-55			38.62	0.232	166.35
1851-57	Beds without		37.62	0.209	1/9./
004-0	ammonoids	Nakhodka reef	33.0181	0.2614	125.312
004-4		- :	31.9081	0.2/01	118.356
054-40			32.1238	0.2688	119.508
1004-0			34.8402	0.2633	132.344
004-1		.	33.00	0.2008	129.33
1054-2		ļ — ¨ —	35.05/2	0.2901	1 113.010
		.1	l	L	1

Table 2 Ca and Mg abundances in the limestones of the Chandalaz Horizon in South Primorie.

Foraminifera: Palaeofusulina.

Brachiopods: Acosarina, Waagenites, Leptodus, Haydenella, Uncinunellina, Araxathyris, Squamularia, Spiriferellina, and Hustedia.

Ammonoids: Pleuronodoceras.

Feixianguan Formation (Lower). 7. Marls, muddy limestones, calcareous mudstones,

shales (Sample N KT-24A, 0.55 m above the base of the formation, in a bed characterized by the Triassic *Claraia griesbachi* (Bittner). Thickness 0.75 m.

Analytical data indicate that the limestones at the base of the Induan Stage (beds with *Claraia*) of the Chongqing area differ from the Permian rocks of the Changxing Formation in the low (negative) values of δ^{13} C (Tables 3 and 4), supporting the results of previous investigations in South China [17], [44], [47], [51].

 Table 3
 Carbon and oxygen isotopic ratio in the Upper Permian brachiopod shells and limestones of the Trans-Caucasia and South China.

Sample	Material	Агеа	Zone, beds (stage, formation)	δ ⁱ³ C (PDB) ‱	δ'" 0 (PDB) ‰	^{δ'*} 0(SMOW) ‰
516-1	Calcite (shell)	Akhura	Hemigordius irregulariformis - Orthotelina axariani, top (Midian)	+1.0	-6.3	
526-6	- " -	Ogbin	Pseudodunbarula orpaensis - Araxilevis intermedium, top (Midian)	+1.3	-5.5	
521-3 437-1 KT- 17	- " - Limestone	Karabaglyar-2 Dorasham-2 Liangfeng (Chongqing)	2 Araxoceras lalissimum (bottom) Araxoceras lalissimum Araxalhyris - Okhamina (Changxiang, member 2)	+2.1 +2.5 +1.4	-6.8 -4.2 -8.5	21.4

 Table 4
 Carbon and oxygen isotopic ratio in the Induan limestones (South China, Trans-Caucasia)

 and ammonoid shells (Primorie).
 Image: Carbon and Car

Sample	Material A	Area	Zone, beds (formation)	δ ^{ι,} C (PDB)	δ ¹ "0 (PDB)	δ ^{1*} 0 (SMOW)
			(committen)	%0	‱	‱
KT- 24 A	Limestone	Liangfeng (Chongqin)	Claraia griesbachi (Fuixianguan)	-1.5	-11.2	+18.7
525-5	- " -	Ogbin	Ophiceras medium, bottom (-*-)	-0.1	-6.4	+23.5
428-4	- " -	Vedi		+0.1	-7.6	+22.3
515-5	- " -	Akhura	Ophiceras medium, top (-"-)	+0.8	-7.5	+22.4
438-15	- " -	Karabaglyar-	1 - " -	+0.5	-9.2	+20.7
525-6	- " -	Ogbin	" -	+0.8	-7.5	+22.4
91- K- 1	Calcite (shell)	Ussuri Bay, Cape Seryi	Gyronikes subdharmus (-*-)	-5.3	-9.9	+20.0
L						

Huangshi

The section of the Permian/Triassic boundary layers in the Huangshi area (Hubei Province) [49] is composed of the following deposits (upward):

Dalung Formation. 1. Mudstones, limestones (KT-33 - 1.2 m, KT-30 - 0.7 m, KT-

31 - 0.5 m below the top of the formation). Thickness 6 m.
 Brachiopods: Crurithyris pigmaea Liao, and Cathayasia sp.
 Ammonoids: Pseudotyrolites, Pleuronodoceras, and Pseudogastrioceras.
 Conodonts: Gondolella subcarinate (Sweet), and Gondolella sp. nov.

Dayhe Formation (Lower). 2. Thinly interbedded limestones and siliceous mudstones (KT-34 - 0.2 m above the base of the formation). Thickness 0.32 m.

3. Thinly interbedded calcareous shales and mudstones. Thickness 2.48 m. Bivalves: *Claraia* sp.

Ammonoids: Lytophiceras sp., and Ophiceras tingi Tien.

Considering that the lower member of the Dayhe Formation (0.32 m) is not characterized by fossils, the Permian/Triassic boundary in this sequence can be drawn either at the base or at the top of this member, according to the first appearance of the Triassic Lytophiceras (the latter seems preferable).

The Ca-Mg ratios in the carbonates of the Permian part of the Dalung and Dayhe boundary layers in the Hubei Province range from 139.905 to 159.180 (Table 5), indicating a higher Mg content in these rocks as compared with the Chandalaz limestones of Mt. Senkina Shapka in South Primorie.

Table 5 Ca and Mg content in the Upper Permian limestones of South China (Hubei Province,Huangshi).

Sample N	Formation (bed)	Ca, %	Mg, %	Ca/Mg
KT- 33	Dalung (1.2 m below the top)	39.066	0.2454	159.18
КТ- 30	Dalung (0.7 m below the top)	39.223	0.2561	153.15
КТ- 31	Dalung (0.5 m below the top)	38.824	0.2644	146.835
КТ- 32	Dalung (0.3 m below the top)	39.144	0.2693	145.335
КТ- 34	Dayhe (0.2 m above the base)	38.761	0.277	139.905

TRANS-CAUCASIA

The Upper Permian in Trans-Caucasia is made up of the Asni (limestones), Gnishik (limestones and muddy limestones), Arpa (limestones and muddy limestones with chert interbeds), Khachik (mudstones, limestones, and cherts), Akhura (limestones, marls, and clays) formations and the basal layers of the Karabaglyar Formation (shales, marls, and

limestones) [13]. The thickness of the Upper Permian in Trans-Caucasia is about 380-410 m.

The highest content of heavy-carbon isotopes was identified in brachiopod shells from the Djulfian Stage [4], [53] (the δ^{13} C values in the Araxoceras latissimum Zone of the Dorasham-2 and Vedi sections reach 2.5‰) (Table 3). Heavy-carbon isotope abundance declines abruptly in the lower part of the Induan beds containing Lytophiceras medium (the δ^{13} C values range between -0.1 and +0.1 in the Vedi and Ogbin sections); in the upper part of these beds it increases slightly (the δ^{13} C values in the Ogbin, Akhura, and Karabaglyar sequences reach 0.5-0.8‰)(Table 4).

Extremely low heavy-oxygen isotope abundances are reported in both Upper Permian and Lower Triassic carbonates (Tables 3 and 4).

The variations in the magnesium abundance in the Upper Permian carbonates of Trans-Caucasia are worth noting. Ca/Mg ratio in the limestones of the lower Gnishik Formation (Murgabian Stage) in the Dzhagadzur area is 166.905; in the middle Gnishik Formation in the Vedi-2 area it is 191.175; in the upper Arpa Formation (lower Midian Stage) in the Dzhagadzur area it is 173.385; in the Hemigordius (Midiella) irregulariformis-Orthotetina azariani Zone of the Khachik Formation (Midian Stage) of the Akhura area, 175.035; the Pseudodunbarula arpaensis-Araxilevis intermedius Zone of the Khachik Formation (upper Midian Stage) in the Ogbin and Vedi areas, 181.350-182.020; the Araxaceras latissimum Zone of the Akura Formation (lower Djulfian Stage) in the Akhura, Karabaglyar-1 and 2, Ogbin, Dorasham-1 and 2, and Kabagly-Chai areas, 180.240 on the average; the Vedioceras ventrosulcatum Zone of the Akhura Formation (upper Djulfian Stage) in the Akhura, Karabaglyar, Ogbin, Gortun, and Dorasham-2 areas, 180.660 on the average; the Phisonites triagularis Zone of the Akhura Formation (lower Dorashamian Stage) in the Akhura and Dorasham-2 areas, 181.800-183.180; the Iranites transcaucasius Zone (Dorashamian Stage) in the Dorasham-1 and 2 areas - 187.755-191.700; the Shevyrevites shevyrevi Zone (Dorashamian Stage) in the Akhura, Vedi, and Dorasham-2 areas average 189.470; the Paratirolites kittli Zone of the upper Akhura Formation (Dorashamian Stage) in the Akhura, Avush, and Karabaglyar-2 areas, average 175.900; the Pleuronodoceras occidentale Zone of the lower Karabaglyar Formation (upper Dorashamian Stage) in the Akhura area, 185.329; the base of the beds with Lytophiceras *medium* of the Karabaglyar Formation (lower Induan Stage) in the Karabaglyar-1 and 2, Ogbin, Vedi-2, Karabagly-Chai areas, average 193.470; the upper beds with Lytophiceras medium in the Karabaglyar-2 and Ogbin areas, average 197.920; the middle part of the beds with Gyronites of the Karabaglyar Formation (Induan Stage) in the Avush area -172.617; the upper beds with Gyronites in the Karabaglyar-1 area, 199.305 (Table 6). The highest Ca-Mg ratio in the sequence was identified in the beds with Lytophiceras medium of the Induan Stage.

Sample N	Formation (zone)	Locality ждение	Ca, %	Mg. %	Ca/Mg
1	2	3	4	5	6
507-2	Gnishik (lower)	Dzhagadzur	38.811	0.2325	166.905
429-9	Gnishik (middle)	Vedi-2	36.933	0.1932	191.175
506-2	Arpa (upper)	Dzhagadzur	37.313	0.2152	173.385
516-2	Khachik (Hernigordius irregularifor -	Akhura	37.722	0.2155	175.035
ł	mis - Orthotelina azarjani)				
522-3	Khachik (Pseudodunbarula arpaen -	Vedi-1	38,188	0.2098	182.020
	sis - Araxilevis intermedius)				
526-6		Oghin	38.002	0.2095	181.350
513-1	Akhura (Araxoceras latissimum)	Akhura	38.112	0.2187	174.266
525-2		Ochin	38,544	0.2164	178.576
526-7	- · _	Ogbin	37.558	0.2067	181.635
431-1		Dorasham-2	37.214	0,1928	192.990
521-4	_ • _	Karabagiyar-2	37.850	0.2143	176.580
513-2		Akhura	38.452	0.2254	170,520
447-1	_ · _	Kabagly-Chai	38.003	0.2111	180.000
435-7		Dorasham-1	37.800	0.2120	178.290
439-1a	- • -	Karabaglyar-1	37.426	0.1952	191.670
439-1	- • -	Karabagiyar-1	37.388	0.1940	192.705
521-4	_ · _	Karahagiyar-2	37.850	0.2143	176.580
521-5			38.020	0.2202	172.661
521-2			37.953	0.2144	177.00
526-3	Akhura (Vedioceras ventro- sulcatum)	Ogbin	37.718	0.2204	171.134
440-4	Akhura (Vedioceras ventrosul-	Karabaglyar-2	37.881	0.2020	185.070
441-4	_ · _	Karabaalwar 2	37.683	0,1978	190.500
514-5	_ · _	Akhura	37.660	0.2044	183,900
514-8	- · _	Akilura	37.888	0.2104	180.000
524-1	_ • _	Gortun	37.896	0.2210	171.475
431-9	Akhura (Phisonies triangularis)	Dorasham-2	37.289	0.2051	181.800
514-16	_ • _	Akbura	37.672	0.2056	183.180
434-13	Akhura (Iranites transcaucasius)	Dorasham-1	37.681	0.1965	191.700
433-3	- · -	Dorasham-2	37.884	0.2017	187.755
433-9a	Akhura (Shevyreviles shevyrevi)	- · -	37.847	0.2044	185.145
433-9b	_ · _	[_ " <u>_</u>	37.383	0.2094	178.470
522-5	_ · _	Vedi-1	37.930	0.2060	184.050
515-1	- · -	Akhura	37.458	0.1969	190.230
517-3	Akhura (Paratirolites kittli)	Avush	37.562	0.2208	170.118
514-32	_ · _	Akhura	38.440	0.2223	172.379
515-2	_ · _		37.903	0.2069	179.164
514-12		- "	37.998	0.2180	173.685
514-5			37.624	0.2040	184.431
514-32			38.428	0.2213	173.640
518-6		Karabagiyar-2	38.029	0.2238	169.924
518-7		_ * _	37.338	0.2074	179,970
	l	,			

 Table 6
 Ca and Mg content in the Upper Permian and Lower Triassic limestones of Trans-Caucasia and the North Caucasus.

1	2	3	4	5	6
526-3	Akhura (Paratirolites kittli)	Ogbin	37.938	0.2095	181.005
432-2		Dorasham-2	37.553	0.2052	182.955
515-5	Karabaglyar (Pleuronodoceras	Akhura	38.011	0.2051	185.329
ł	occidentale)			[
424-1	Urushten	Raskol Massif	37.400	0,1935	193.290
		Cliff (Belaya R.)			
438- 11	Karabaglyar (Lytophiceras	Karabagiyar-2	37.210	0.1820	204.255
	medium)]		
438-9		"	37.861	0.1920	197.055
518- 2a	— " —	- " -	38.200	0.2191	174.300
518-2		- " -	38.120	0.2168	175.830
428-4		Vedi-2	37.400	0.1934	193.290
525-6		Ogbin	38.012	0.2231	170.380
441-2	Karabaglyar (Lytophiceras	- • -	37.121	0.1852	200.340
1	medium)				
441-3	- • -	- "	37.017	0.1753	211.080
517-5	Karabaglyar (Gyronites)	Avush	37.786	0.2189	172.617
438- 15	Karabaglyar (Gyronites)	Karabaglyar-2	37.353	0.1870	199.305

Table 6(continued).

CORRELATION OF THE UPPER PERMIAN AND LOWER TRIASSIC DEPOSITS ACCORDING TO VARIATIONS IN CARBON-ISOTOPIC COMPOSITION

Two major changes in the abundances of heavy carbon isotopes in the Upper Permian and Lower Triassic carbonates are worthy of note.

The first is the anomaly first discovered in the Zechstein basin (in Germany and England) [41]. It was identified in the basal layers of the Zechstein sequence (Kupferschiefer, Marl Slate) [36], [41] enriched in organic matter ($C_{org} = 5\%$) and with high Cu, Pb, and Zn concentrations. The δ^{13} C values in the marl slates of the English Zechstein amount to 5.2‰. The age of the basal layers of the Zechstein sequence, according to a conodont of the genus *Merrillina* [34] discovered there, is not older than the top of the Abade Formation in Iran and not younger than the lower Djulfian Stage in Trans-Caucasia.

The highest δ^{13} C (ranging from +2.5 to +3.5%) in the Carnic Alps were identified in the carbonates of the lower unit (IA) of the Bellerofont Formation [28], [31], [38], [39] of probable Djulfian age. Data on the isotopic composition of the deposits underlying this formation are not available (they are composed of mostly sandy facies).

The highest δ^{13} C values in the Upper Permian of Trans-Caucasia (2.1-2.5‰), as mentioned above, were detected only in the beds of the lower Djulfian Stage, characterized by occasionally high phosphorus content (up to 1.67-1.20% of P₂O₅). The precise position of the layers corresponding with the appearance of the Zechstein anomaly, as in the case of the Southern Alps, is not specified here. In Texas the Upper Permian anomaly corresponds with the upper part of the upper unit (Claystone III) of the Bell Canyon Formation of the Guadalupian Group and the lower units of the Castile Formation of the Ochoan Group (Basal limestone, Anhydrite I) [24], [37]. At the top of the Guadalupian Group (Upper Capitanian), the δ^{13} C values amount to more than 3‰; in the lower Ochoan Group (basal limestone) it varies widely not exceeding 2.5‰; in the lower part of the next unit, δ^{13} C = 6.5‰ [37]. Abnormally high abundances of heavy isotopes remain within the rest of the formation, probably corresponding with the Djulfian Stage (along with a low C_{ore} content).

In the lower part of the sequence (Bell Canyon Formation, excluding the uppermost beds) the δ^{13} C values are "normal" (between -2.5 and +1.8 ‰).

Consequently this carbon-isotopic anomaly appeared in Texas no earlier than the end of the Capitanian (Midian) and continued until at least the early Djulfian.

Abnormally high δ^{13} C values (3.6-4.1%) in South Primorie, as mentioned above, were recorded at the top of the *Neomisellina lepida-Lepidolina kumaensis* Zone (members 10-13) and in the overlying deposits in the interval between the beds without ammonoids and the beds with *Xenodiscus subcarbonarius* of the Nakhodka reef.

The first appearance of abnormally high heavy-carbon isotope abundances at the base of the Zechstein Group in Germany (Kupferschiefer) and England (Marl Slate), in the upper Capitanian (Bell Canyon, Claystone III) in Texas, at the top of the *Metadoliolina lepida-Lepidolina kumaensis* in South Primorie, and possibly at the base of the Bellerofont Formation in the Southern Alps probably reflects a synchronous (late Capitanian) event. It is not inconceivable that the anomaly ($\delta^{13}C = 4.5-7.5 \%$) recently identified in the middle Cape Starostin Formation on Spitsbergen [25] corresponds with the same chronostratigraphic level. The carbon-isotopic anomaly discussed is obviously one of the most significant in the Phanerozoic.

The cavernous Permian dolomites of the Zechstein sequence are known to contain considerable oil reserves. Probably this is largely due to the intense accumulation of C_{org} during the late Capitanian-early Djulfian. In this connection, the carbonate deposits of this age in other regions of the world are apparently petroleum prospective. It should be noted that the thick Chandalaz limestone sequence of South Primorie is strongly karstified, the limestones are in places bituminous, and the carbonate sequence is overlain by mudstones, and all these features are indirect indicators of the presence of petroleum.

Another important late Permian-earliest Triassic event is the abrupt decline in carbonisotope abundance in the Permian/Triassic boundary layers, often accompanied by platinum-group elements (Ir, Co, Cr, and Ni) and other metals (As, Se, and Sb, etc.) [31], [51], which can also be taken into account for their detailed correlation.

As was mentioned above, extremely low δ^{13} C values (-1.5‰) in the Chongqing section of South China have been detected 0.55 m above the bottom of the Feixianguan Formation (beds with *Claraia griesbachi*) in obviously Induan deposits. According to the published data [47], [51], the minimum δ^{13} C digression (-6.0‰) in the Meishang

section, suggested as the Permian/Triassic boundary stratotype, corresponds with the lower 6-cm thick interval of bed 27 (mixed bed 2) of the Yinkeng (Qinglung) Formation, with a total thickness of 16 cm. Immediately above this part of the bed, the conodont *Hindeodus parvus* (Kozur et Pjatakova) was discovered, and these beds were assumed to be the basal layers of the Triassic [51]. The δ^{13} C values in the underlying beds 26 and 25 (mixed bed), of the same Yinkeng Formation, range around zero, and in the upper part of the older Changxing Formation they are considerably higher (reaching +2‰) [51]. Iridium and other elements are extremely unevenly distributed in the Permian/Triassic boundary beds (the existence of an iridium anomaly here lacks support). A small iridium peak was discovered only in a 1 cm interval of the topmost part of bed 26 [47], [51].

In the Trans-Caucasian Permo-Triassic the lowest abundance of heavy-oxygen isotopes was discovered in the lower part of the Induan beds with *Lytophiceras medium* (the δ^{13} C values range between -0.1 and +0.1%); in their upper part, δ^{13} C = 0.5-0.8%. The Permian/Triassic boundary beds here show only low iridium abundances (0.004-0.039 ppm); the most significant peak in the Sovetoshen section was detected approximately 10 cm below the bottom of the algal limestones [16] which corresponds with the level at which the last Permian brachiopods (*Haydenella* sp.) of the *Pleuronodoceras occidentale* Zone were found [54].

The upper Djulfian and Dorashamian deposits and the Permian-Triassic boundary beds, which outcrop throughout the vast Trans-Caucasian territory, are mostly red (enriched in Fe).

In the Carnic Alps (Gartnerkofel), the δ^{13} C values in the upper Bellerofont Formation and in the lower Tesero Horizon of the Werfenian sequence are +1.0-1.5 ‰, falling to -1.0‰ in the upper part of the horizon [31]. In the lower (3A) member of the Mazzin unit of the Werfenian sequence, three abrupt minimuma of heavy-carbon isotope abundance have been reported. The first one (δ^{13} C = -1.5 ‰) was detected 5 m above the top of the Tesero Horizon; the second (δ^{13} C = -0.6‰), 35 m above it; and the third (0.9‰), 39 m above the top of that horizon. The δ^{13} C value in the overlying Werfenian deposits reaches 1.3 ‰ [31].

High iridium abundances in a well drilled in the Gartnerkofel area was detected at two levels within the Werfenian sequence. The lower peak (165 ppm) was detected at the top of the Tesero Horizon, 4.5 m below a bed with extremely low $\delta^{13}C$ content (-1.5%). The upper peak (230 ppm) was identified in a bed located 40 cm above the level characterized by the third lowest $\delta^{13}C$ value (-0.9%) [31].

An extremely low heavy-carbon isotope content was discovered in the shells of late Dorashamian brachiopods of the Cape Starostin Formation in West Spitsbergen [25] and the Permian/Triassic boundary layers in Greenland [42]. These sequences require a further detailed study.

On the basis of the above data, the most logical position of the Permian/Triassic boundary in South China corresponds with the bottom of bed 27 (mixed beds) of the

Yinkeng (Qinglung) Formation, at the bottom of which a minimum δ^{13} C digression (-6.0‰) was identified, or somewhat higher (8 cm above the bottom of that bed), where the first appearance of the *Hindeodus parvus* conodonts is inferred. In Trans-Caucasia it probably corresponds with the top of the *Pleuronodoceras occidentale* Zone [5], [54], considering the associated small iridium peak and the details of *Hindeodus parvus* distribution in the sequence. The precise location of the Permian/Triassic boundary in the Carnic Alps of Austria offers some difficulties, considering the occurrence of several levels with low δ^{13} C values and high abundances of iridium and other trace elements. The Permian/Triassic boundary in the Alps might be drawn in the lower part of the Mazzin unit of the Werfenian sequence, where the lowest δ^{13} C value was identified and where H. Kozur reported the first appearance of the conodont *Hindeodus parvus*, but that would be contradictory to some of the fossil data published by H. P. Shonlaub [43].

ENVIRONMENTAL CONDITIONS AT THE PERMIAN-TRIASSIC BOUNDARY

A huge amount of information has been accumulated in support of the concept that high heavy-carbon isotope abundances in the Permian sediments are indicative of high C_{org} abundance in the late Permian ocean, whereas the abrupt decrease in δ^{13} C values in the Permian/Triassic boundary beds coincides with the reduced accumulation of C_{org} and the development of anoxic conditions [2], [17], [18], [25], [26], [27], [28], [29], [30], [31], [35], [37], [38], [39], [40], [41], [42], [45], [51]. At the same time the problems of climatic change in the earliest Triassic remain a matter for extensive discussion.

There are two opposing opinions on the mechanism responsible for the high CO_2 concentration in the Permo-Triassic atmosphere producing the hothouse effect and consequently a rising temperature.

W. T. Holzer and M. Gruszczynski *et al.* [17], [25], [27], [28], [29], [30], [31], [37], [38], [39] explain the inferred high CO_2 concentration in the atmosphere during the period between the Permian and Triassic by mass carbon oxidation under conditions of marine regression.

Many scientists [2], [21], [22], [50] advocate the concept of the leading role of volcanic activity in the atmospheric CO₂ balance. At the same time, various authors disagree about the timing of the major Permo-Triassic climatic events. M. I. Budyko [2] suggests cooling during the latest Permian to early Triassic in response to the reduced volume of volcanic rocks in this interval of the Phanerozoic. I. Campbell *et al.* [21] and Canaghan *et al.* [22], on the contrary, attach much importance to the Siberian trap eruptions that they deem coeval with correct dating of the Permian/Triassic boundary (251.2 ± 3.4 Ma [51]). This event, in their opinion, accounts for emissions of dust and volcanic SO₂ emissions into the atmosphere, resulting first in a short-term cooling (associated with a sea-level lowstand) and then followed by a long-term warming of

climate in response to the hothouse effect and marine transgression.

As an argument against Holzer and Gruszczynski *et al.* [17], [25], L. A. Berner [18] explains the abrupt decrease in the δ^{13} C value in the sea-water and biogenic carbonates and low oxygen concentrations in the atmosphere during the period between the Permian and Triassic, basically as the effect of the arid climate at that time, resulting in reduced photosynthesis on the continent, which led to a considerably reduced supply of organic matter into the ocean. At the same time, M. Magaritz *et al.* [37], [40] draw our attention to the fact that high δ^{13} C values were also detected in the carbonate intervals of the evaporite sequences of Texas and the West European Zechstein basin, although high heavy-carbon isotope abundances in the Upper Permian sediments of these regions first appeared long before evaporite accumulation.

The specific diagenetic features of the carbonate biogenic remains in the known Permian/Triassic boundary sections give no way of using the most reliable oxygen-isotopic method for the solution of the problems concerning the temperature conditions during the period between the Permian and Triassic (the detected δ^{13} C values enable calculation of obviously impossible paleotemperatures [25], [52]).

Specific investigations [8], [11], [14] indicate that the Ca-Mg method, suggested by T. S. Berlin and A. V. Khabakov [1] for paleotemperature estimates on the basis of carbonate biogenic remains or host rocks, cannot be used as suggested, because of the complex dependence of Ca/Mg ratios in sea-water and in the skeletons of marine organisms upon a number of physicochemical features of these media. In the opinion of a number of scientists [19], [23], dolomitization of the carbonates laid down in waters of normal salinity is to a certain extent related to the transgressions characterized by high pCO_2 values.

Corresponding with the periods of marine transgression in Trans-Caucasia (in this case probably during a climatic optimum, considering the taxonomic variety of the Permian biota), are the Gnishik, upper Arpa, lower Djulfian, and some upper Dorashamian carbonates (the *Paratirolites kittli* Zone) [52]; it appears that these rocks show the highest values of magnesium content as compared with the other Upper Permian deposits.

Considering that the lowest Mg content in the sequence was identified in the basal layers of the Lower Triassic (beds with Lytophiceras medium) and that the widest variations in the Ca/Mg ratio were detected in the overlying beds with Gyronites, one may suggest that it is precisely the Lytophiceras medium zonal moment, characterized in Trans-Caucasia by an abrupt decrease in the heavy-carbon isotope abundance in the sea-water that corresponds with the peak of the latest Permian to Early Triassic lowstand and climatic cooling. The inferred regression at the Permian/Triassic boundary probably accounts for the increased aridity of the climate that began by the end of the Djulfian and continued into the Induan, taking into account the accumulation of evaporites in the Western European Zechstein basin [36] and Texas [37], and the data on phosphatogenesis [56]. We have no marked evidence of the development of a warm, humid climate during

the earliest Triassic, as assumed by a number of investigators [31]. A small karst-type bauxite show in Trans-Caucasia [3] and the products of weathering (siallitic residue) in the Southeast Pamir [13] were developed after the Permian rocks, the upper Dorashamian age of which is not proved.

The increasing aridity of climate, which resulted from a considerable regression and the abrupt cooling of climate, probably account for the unprecedented reduction in the amount and taxonomic variety of the major organic groups at the Permian/Triassic boundary, followed by the extinction of a great number of forms (fusulinids, rugose corals, productids, goniates, trilobites, many amphibian, reptilian, and plant groups [53] and whole ecosystems (e.g. reef systems). The problems were intensified by the abrupt decrease in oxygen content in the atmosphere and the ocean in response to the extinction of a large proportion of the photosynthesizing organisms.

The role of the arid climate in the suggested model of development of the late Capitanian-Djulfian carbon-isotopic anomaly and the abrupt drop of δ^{13} C at the Permian/Triassic boundary is not absolutely clear. However, time delay between the climatic changes and changes in sea-water isotopic composition seems natural. Also one cannot assume that the climate was stable during Djulfian-Dorashamian times (a rapid succession of arid and humid conditions at the end of the Permian might just as well have taken place).

The warming up of climate after the changes that took place at the Permian/Triassic boundary may have begun by the end of the Lytophiceras medium zonal moment of the Induan, associated with a certain increase in the Mg content in the carbonates of the Tethyan province; but a considerable increase in the oxygen content of the water probably did not occur earlier than the beginning of the Olenekian. It was only then that the ammonoids attained their former abundance and taxonomic variety, proving to be more progressive in this respect than the other organisms that they outlived. In this regard, authors [21], [22] who associate short-term abrupt cooling at the beginning of the Induan, followed by warming, with the trap intrusions of Siberia (U/Pb age of zircons, 248 \pm 4 Ma; Ar age of biotites, 249 + 1.6 Ma [22]) are probably correct in their assumption. The absolute age of the Emeishang basalts in West China is 230-280 Ma [7], but many of them were erupted during the Late Permian [50]. Acid and intermediate volcanic deposits (ash and tuff) have been identified immediately in the Permian/Triassic boundary beds over the vast South China territory (Sichuan, Hunan, Guangxi, Fujian, Zhejiang, and Hubei, etc.) [5] and in the upper Dorashamian Stage of the Permian sequence in South Primorie [55].

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