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The Guadalupian (Permian) Kamura event in European Tethys

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ABSTRACT

In order to document paleoenvironmental conditions of the equatorial western Paleo-Tethys during the late Middle Permian prior to the end-Guadalupian mass extinction, chemostratigraphic analysis using stable carbon isotopes was conducted for the Guadalupian rocks at Brusane in the Velebit Mtn., central Croatia. By analyzing 72 carbonate samples of the Capitanian (Upper Guadalupian) Velebit Formation, we found an interval with unusually high $\delta^{13}C_{carb}$ values (+4 to +6‰) in the ca. 150 m-thick *Yabeina* (fusuline) Zone. The present find clarifies that the primary productivity and burial rate into the sediments were considerably high during the Capitanian in westernmost Paleo-Tethys. This chemostratigraphic signal is properly correlated with the "Kamura event" detected in a mid-Panthalassan paleo-atoll limestone in Japan. The present results identify the Capitanian "Kamura event" for the first time in European Paleo-Tethys on the opposite side of the globe from the mid-Panthalassan paleo-seamount, and prove the global context of the event as well as its utility in chemostratigraphic correlation. In order to enhance bioproductivity on a global scale, the increase in nutrient supply is inevitable. In addition to riverine run-off from Pangea, active oceanic circulation, in particular upwelling of deep-sea water enriched in nutrients, was likely vital both in Panthalassa and Paleo-Tethys. The extinction of some Guadalupian fauna, in particular photosymbiotic community (large-tested fusulines, large bivalves, rugose corals), was likely related to a temporary cooling coupled with eutrophication in low-latitude shallow marine environments of Paleo-Tethys and Panthalassa.

1. Introduction

The end-Paleozoic biological crisis was the biggest event in the Phanerozoic life history, as the evolutionary trend exhibited a replacement of the Paleozoic Fauna with the Modern Fauna (e.g., Erwin, 2006; Bottjer et al., 2008). The double-phased mass extinction, first at the Guadalupian–Lopingian (Middle–Late Permian) boundary (G–LB) and second at the Permo–Triassic boundary (P–TB), was originally pointed out by Stanley and Yang (1994) and Jin et al. (1994). Before their notice, the G–LB event was not a main research target because of the more impressive P–TB event; however, this event became widely known and various studies have been conducted during the last decade (e.g., Weidlich, 2002; Isozaki et al., 2004; Shen and Shi, 2009; Clapham et al., 2009; Wignall et al., 2009). The G–LB event is unique in having various geological phenomena of global scale in addition to the major change in biological communities; i.e. the lowest sea-level in the Phanerozoic (Haq and Schutter, 2008), the lowest $^{87}Sr/^{86}Sr$ ratio in the Phanerozoic (e.g., Veizer et al., 1999; McArthur and Howarth, 2004; Korte et al., 2006; Kani et al., 2008), and a sharp trend change in geomagnetic polarity reversal (e.g., Ogg, 2004; Steiner, 2006; Isozaki, 2009a). Furthermore, it is noteworthy that the onset of volatile carbon isotope fluctuations and the overall oxygen depletion in the superocean Panthalassa across the P–TB started close to this timing (Isozaki et al., 2007b, Isozaki, 1997). Summarizing all these geologically rare thus "strange" phenomena, Isozaki (2009b) emphasized that the transition from the Paleozoic world to the Mesozoic one had started not at the P–TB but at the G–LB. The cause(s) has not been fully detected; however, many researchers discuss terrestrial causes, such as activity of large igneous provinces (e.g., Courtillot, 1999; Ali et al., 2002; Zhou et al., 2002; Isozaki, 2009b; Wignall et al., 2009), rather than extraterrestrial impact like the end-Cretaceous case. Nonetheless, a different connection possibly to the extra-solar system was recently pointed out for the trigger of the late Middle Permian global event (Isozaki, 2009b).

Study of stable carbon isotope ratios of shallow marine carbonates is a standard approach to the major mass extinction-related boundary events. Numerous data for the P–TB event have been published since the first attempt by W.T. Holser and his group (e.g., Holser et al., 1989; Baud et al., 1989). Also for the G–LB, further chemostratigraphic studies identified a negative shift in C isotope ratio that might be related to the first extinction (e.g., Wang et al., 2004; Kaiho et al., 2005). On the other hand, Korte et al. (2005) demonstrated the secular trend of C isotope ratio of the seawater during the Permian. Recently another interesting C isotope episode with extremely high positive $\delta^{13}C_{carb}$ values

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over +5.0‰ was recognized in a mid-Panthalassan paleo-atoll limestone in Japan; i.e. the late Guadalupian Kamura event possibly linked to the late Guadalupian biodiversity decline (Isozaki et al., 2007a). As the under- and overlying units lack such a unique signal (Wang et al., 2004; Isozaki et al., 2007b; Musashi et al., 2010), this can be utilized as a prominent tool in global chemostratigraphic correlation.

In order to examine whether or not the Kamura event was a global phenomenon of the late Guadalupian, we conducted a stable carbon isotope study on the Upper Guadalupian shallow marine carbonates (the Velebit Formation) in the Velebit Mountains in central Croatia. During the Permian, the Velebit Mountains were located at the western dead-end of the Paleo-Tethys around the paleo-equator (e.g., Gaetani et al., 2003; Muttoni et al., 2009; Fig. 1), i.e. almost at the opposite side of the globe with respect to the mid-Panthalassan paleo-seamount (Ota and Isozaki, 2006; Kirschvink and Isozaki, 2007) where the Kamura event was first detected, thus the study area represents an ideal area to check the putative global nature of the Kamura event. This article reports our first find of an interval of extremely high positive $\delta^{13}C_{carb}$ values in the Capitanian part of the Guadalupian Velebit Formation. We discuss its geological significance with respect to the global environmental change, in particular, global cooling during the Capitanian and the relevant extinction of some tropical fauna.

2. Geologic setting

The External Dinarides are composed mostly of Mesozoic to Paleogene platform carbonates, developed along the westernmost part of the Tethys, that is often called Adriatic Carbonate Platform (e.g., Vlahović et al., 2005). The Velebit Mountains in central Croatia (Fig. 2) is an exceptional part of the External Dinarides, where we can observe an extensive occurrence of Upper Paleozoic sedimentary rocks, in particular, Middle-Upper Permian carbonate rocks (e.g., Salopek, 1942; Kochansky-Devidé, 1965; Sokač et al., 1976; Aljinović et al., 2003; Sremac, 2005). The Permian rocks in the Velebit Mountains comprise three distinct stratigraphic units; i.e., the Sakmarian (Early Permian) Rattendorf Beds (carbonate), probable Middle Permian clastic Košna Formation, and the Middle-Upper Permian Velebit Formation (carbonates) in ascending order (Kochansky-Devidé, 1982; Flügel, 1977).

The Velebit Formation, ca. 900 m thick, is composed mainly of dolostone with three major horizons of limestone (Fig. 2); the lower, middle and upper limestones that yield various fossils, such as gastropods, bivalves, brachiopods, cephalopods, rugose coral, sponges, bryozoans, fusulines, smaller foraminifers, and calcareous algae, of typical Tethyan characteristics (Herak and Kochansky-Devidé, 1960; Kochansky-Devidé, 1965, 1978, 1979, 1982; Sremac, 1991). The rock types and fossil content suggest that the Velebit Formation was formed in a shallow marine setting, on a continental shelf along the low-latitude northern margin of Gondwanaland (Fig. 1). The lower, middle, and upper limestones are characterized by the following 3 fusuline assemblages in ascending order, respectively; the *Eoverbeekina salopeki* Zone, *Neoschwagerina craticulifera* Zone, and *Yabeina syrtalis* Zone (Kochansky-Devidé, 1965). These 3 zones are currently correlated with the Artinskian (Late Cisuralian), Wordian (or Murgabian+ early Midian; Middle Guadalupian), and Capitanian (or middle-late Midian; Late Guadalupian), respectively (Aljinović et al., 2008). To date, no conodonts were recovered, probably owing to the strong facies control to the shallow marine environments.

The studied section around the Velnačka glavica hill in Brušane on the south of a small stream (44° 29′ 41″ N, 15° 16′ 04″ W) exposes the upper part of the Velebit Formation (Salopek, 1942) (Fig. 2). The Brusane section is about 250 m thick, composed mostly of light gray dolostone with 3 distinct black argillaceous limestone lenses, i.e., L-1 (45 m), L-2 (11 m), and L-3 (37 m) in ascending order (Fig. 3). Sremac (1991) described detailed lithofacies of L-1, and Aljinović et al. (2008) recently confirmed the biostratigraphy of this section. All these 3 limestone units belong to the *Yabeina syrtalis* Zone of Capitanian age (Aljinović et al., 2008). More details of lithofacies of the entire section will be reported elsewhere.

The preservation of primary sedimentary structures and fossils are considerably better in black limestone than in light gray to white

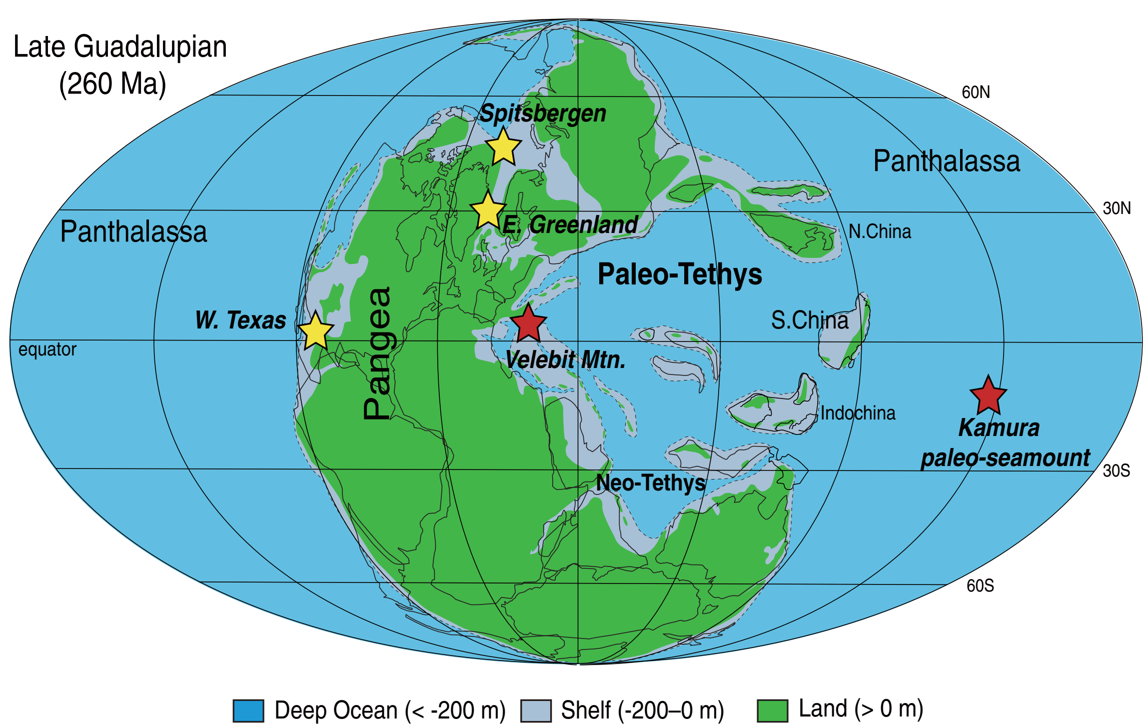

Fig. 1. Late Guadalupian paleogeographic map (based on Ziegler et al., 1997 and modified according to Maruyama et al., 1989, Gaetani et al., 2003, and Muttoni et al., 2009) showing the relative positions of the Velebit Mtn. (Croatia), Kamura paleo-atoll (Japan), West Texas, East Greenland, and Spitsbergen that recorded the Guadalupian high positive $d^{13}C_{carb}$ interval (the Kamura event). Note that the Velebit Mtn. in western Paleo-Tethys and the mid-Panthalassan paleo-seamount were located on the opposite sides of the Earth from each other, and that West Texas, Greenland, and Spitsbergen were separated from Paleo-Tethys and faced to Panthalassa during the Permian.

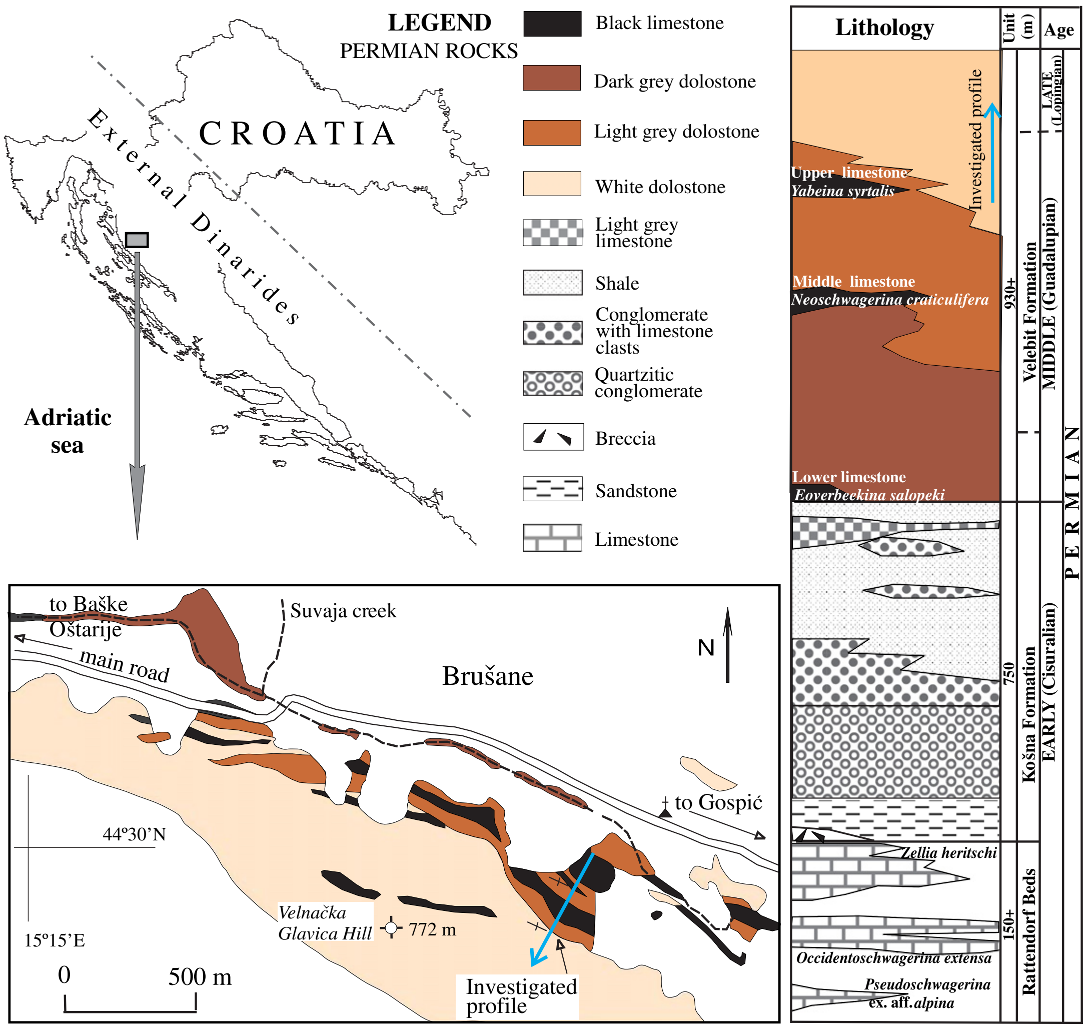

Fig. 2. Index and geologic sketch maps of the Brušane area and simplified stratigraphic column of the Permian rocks in the Velebit Mountains, central Croatia (modified from Salopek, 1942; Kochansky-Devidé, 1979). This study focuses on the upper limestone unit of the upper Velebit Formation. The upper limestone in fact consists of 3 limestone units, i.e. L-1. L-2, and L-3 in ascending order, as illustrated in Figs. 3 and 4.

dolostones. The black limestone is thickly bedded and mainly composed of wackestone and packstone with minor amount of lime mudstone. The black limestone has TOC around 0.9 wt% in average (Aljinović, unpublished data). Coarse-grained parts contain centimeter-size bioclasts of bivalves, rugose corals, bryozoans, and mm-size fusulines and algaes. Some dolostones near the conact with limestone show faint remnants of primary algal structures but most of the dolostones were replaced by coarse-grained dolomite crystals by secondary diagenesis.

3. Samples and analytical methods

We collected samples of unaltered black limestone from the L-1, L-2, and L-3 together with associated dolostone from the upper part of the Velebit Formation at Brušane for stable carbon and oxygen isotope measurements. The carbonates of the Brušane section are free from metamorphism but are partly altered in particular by dolomitization. During the sampling in the field, we intended to collect lime mudstone and micritic parts of wackestone, and avoided coarse-grained parts. In addition, those with strong weathering and/or with many calcite veins were also screened out. As suggested by Brand (2004), the dolomitization could have modified the original stable isotopes of carbonates. Regarding limestone samples, therefore, we carefully eliminated the dolomitized part and then analyzed the relatively fresh part.

We collected 63 limestone samples in total, i.e., 19 from L-1, 9 from L-2, 35 from L-3, and 9 samples of dolostone/dolomitic limestone from horizons adjacent to the black limestone. The stratigraphic levels of the samples are shown in Table 1 and Figs. 3 and 4. Samples of K-1 to K-30 correspond to those reported by Aljinović et al. (2008), and others were newly collected for this study. In order to avoid bioclast-dependent heterogeneity in limestone, fine-grained portion (lime mudstone and micritic parts of wackestone) from each sample was selectively milled by microdrill after examining under the microscope. Approximately 100 μg of the aliquot samples were reacted with 100% H_3PO_4 at 90 °C in an automated carbonate device (Multiprep) coupled with a Micromass Optima mass spectrometer at the Geological Survey of Japan, AIST. Here, $\delta^{13}C = [(^{13}C/^{12}C_{sample} / ^{13}C/^{12}C_{standard}) - 1] \times 1000$, and $\delta^{18}O = [(^{18}O/^{16}O_{sample} / ^{18}O/^{16}O_{standard}) - 1] \times 1000$. All isotopic data are reported as per mil (‰) relative to Vienna Pee Dee belemnite (V-PDB) standard. The internal precision was 0.03‰ and 0.04‰ (1σ) for $\delta^{13}C$ and $\delta^{18}O$, respectively, based on replicate measurements of 23 consecutive samples of the NBS-19 calcite standard (Suzuki et al., 2000).

4. Results

Table 1 lists all the 72 measurements of $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ from the Brušane section. Fig. 4 shows stratigraphic changes in $\delta^{13}C_{carb}$

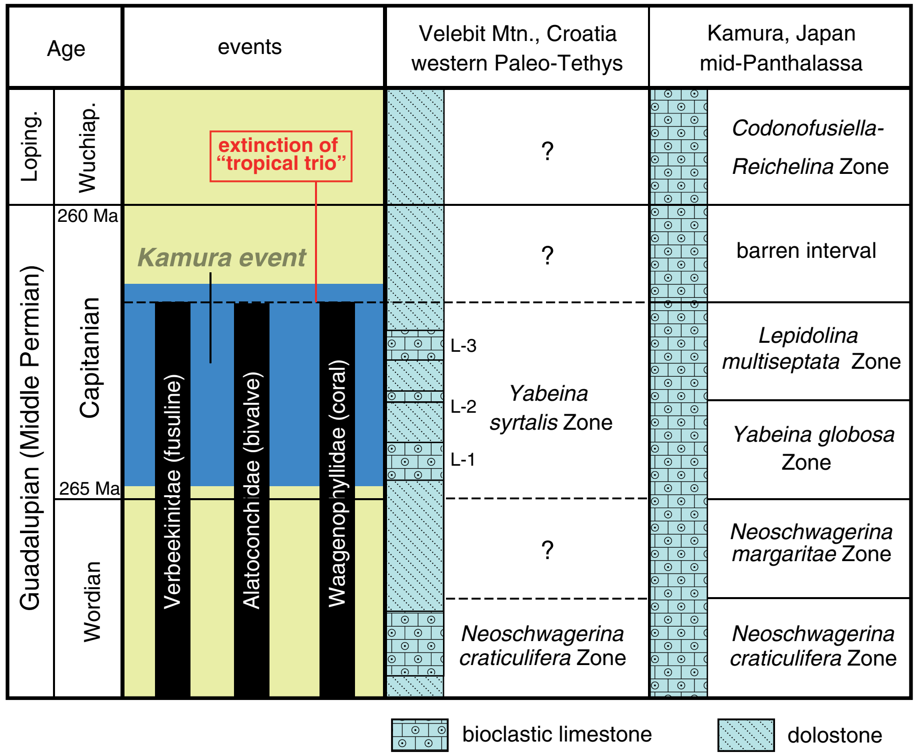

Fig. 3. Correlation of the late Guadalupian fusuline zones and other geologic events of the Velebit Formation in the western Paleo-Tethys and the mid-Panthalassan Kamura paleo-atoll limestone in Japan (compiled from Ota and Isozaki, 2006; Aljinović et al., 2008). Note that the 3 limestone units (L-1, L-2, and L-3) of the upper Velebit Formation all belong to the *Yabeina syrtalis* Zone that is correlated with the Capiatanian in West USA.

values plotted along the column of the study section. All of the $\delta^{13}C_{carb}$ values are positive, whereas all of the $\delta^{18}O_{carb}$ values are negative except one sample.

Most of black limestone samples (filled circles) show positive $\delta^{13}C_{carb}$ values between +4.0 and +5.5‰, with the highest at +5.96‰ (Sample L3-18.2) (Fig. 4). On the other hand, most samples of dolostone and dolomitic limestone (open circles) have relatively lighter $\delta^{13}C_{carb}$ values (< +4.3‰) than those of the limestone samples. Judging from the obvious diagenetic overprint in dolostone, the following discussion on the primary isotopic signals stays solely with isotopic data from limestone samples.

Regardless of some minor fluctuations, the limestones of the upper Velebit Formation are curbed roughly in the 2‰ range between ca. +4.0 and +6.0‰ throughout the section. The most important feature is that the general trend is obviously on the high positive side. Therefore we believe that the $\delta^{13}C_{carb}$ profile may represent the primary signal in spite of partial influence by secondary diagenetic effects. An exceptional volatile change for nearly 4‰ is observed at the topmost L-3 (samples K-28, L3-17-1, L3-17-2, L3-17.1, K-29, L3-18.1, L3-18.2 from ca. 1.5 m-thick interval) immediately below the contact between the black limestone to the overlying dolostone (Fig. 4). Microscopic observation confirmed that this part was slightly affected by dolomitization.

In general, secondary diagenetic effects drive $\delta^{13}C_{carb}$ to lower values; therefore, the high positive $\delta^{13}C_{carb}$ values in L-1, L-2, and L-3 likely represent the primary isotopic signature even with secondary diagenetic overprint in part. Under the circumstances, it is reasonable to regard the outer envelope of $\delta^{13}C_{carb}$ values on the high value side as the approximate original C-isotope profile of the upper Velebit Formation (Fig. 4). This outer envelope, fluctuating between +5.0 and +6.0‰, does not show any overall increasing or decreasing trend. The minor fluctuations might derive possibly from submicroscopic-scale heterogeneity in limestone samples, although we intended to select fine-grained lime mudstone parts and avoided coarse-grained bioclasts during milling.

The $\delta^{18}O_{carb}$ values of limestone samples range in −1.2 to −8.9‰ with one exception (K-15; +0.85‰) (Fig. 4). The samples of dolostone and dolomitic limestone have $\delta^{18}O_{carb}$ values ranging mostly in −1.0 to −7.0‰. The $\delta^{18}O_{carb}$ values are relatively concentrated around −6.0‰ in L-1, whereas ranging more widely in lighter values of −6.0 to −8.5‰ in L-2 and L-3. $\delta^{18}O_{carb}$ of carbonate of old limestone was often affected by secondary carbonate that was under influence of terrestrial water, thus we will not discuss the primary $\delta^{18}O_{carb}$ signature of the Permian seawater here.

The overall correlation between $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ is not clear throughout the studied section; thus the two isotope systems behaved independently from each other. The upper one third of L-3, except the uppermost 1 m part, show apparent parallelism (Fig. 4); however, this part is characterized by relatively lighter isotope ratios both in $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ with upward decreasing trend toward the overlying dolostone; thus this part was likely affected secondary alteration associated with dolomitization. If this is the case, the primary $\delta^{13}C_{carb}$ values were possibly much higher. The relatively lower $\delta^{13}C_{carb}$ values at the bottom of L-1 (K-0, K-1) and of L-2 (L2-1) may be explained likewise.

5. Discussion

5.1. High positive $\delta^{13}C_{carb}$ interval in Velebit

The new data demonstrate that the Capitanian fossiliferous black limestones (L-1, L-2, and L-3) of the upper Velebit Formation in central Croatia have relatively high positive values of $\delta^{13}C_{carb}$ above +4.0‰ up to +6.0‰ (Table 1, Fig. 4). The studied three black limestone units all have high positive values, and nearly two thirds of the measurements are over +5.0‰. Despite sporadic lower values probably reflecting a diagenetic overprint, the outer envelope on the high value side, that is restricted roughly between +5.0 and +6.0‰, shows the general secular trend of $\delta^{13}C_{carb}$ values for the black limestones. These high positive

Table 1
Analytical results of $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ normalized to the Vienna Pee Dee belemnite of the Guadalupian Velebit Formation in the Brušane area, Croatia.

Sample	Unit	Horizon (m)	$\delta^{13}C_{carb}$ (‰)	$\delta^{18}O_{carb}$ (‰)
K-0	L-1	0	4.674	−1.633
K-1	L-1	1.2	4.515	−8.073
K-1.1	L-1	4.5	5.867	−8.026
K-2	L-1	7.0	4.388	−6.566
K-3	L-1	14.2	4.632	−3.300
K-3.1	L-1	15.9	5.818	−6.207
K-3.2	L-1	16.6	5.774	−5.904
K-4	L-1	21.0	4.117	−5.677
K-4.1	L-1	24.2	5.479	−5.872
K-5	L-1	28.7	4.109	−5.761
K-5.1	L-1	29.8	4.767	−5.810
K-6	L-1	31.7	4.607	−6.188
K-6.1	L-1	33.5	5.276	−5.948
K-6.4	L-1	36.4	5.463	−6.440
K-7	L-1	38.7	5.205	−5.840
K-7.1	L-1	40.9	5.089	−6.099
K-7.2	L-1	42.1	5.428	−6.331
K-8	L-1	42.4	5.511	−6.426
K-8.1	L-1	43.6	5.509	−6.237
K-9(dol-ls)	L-1	46.6	3.038	−1.305
K-10-1(dol)		49.1	3.798	−4.452
K-10-2(dol)		49.2	3.461	−3.827
L2-1	L-2	0	4.222	−8.039
L2-2	L-2	2.2	4.928	−7.571
L2-3	L-2	3.2	5.280	−7.958
K12-Y	L-2	4.4	4.848	−6.231
K-13	L-2	5.3	5.221	−8.312
L2-6	L-2	6.2	4.655	−7.746
L2-7	L-2	7.0	4.688	−7.808
L2-8	L-2	7.8	4.761	−8.460
L2-11(dol-ls)	L-2	11.4	3.186	−2.316
K-14(dol)		-5.0	4.262	−2.597
K-15	L-3	0	5.341	0.850
K-16	L-3	4.0	4.989	−6.430
K-17	L-3	8.8	4.497	−7.504
K-18	L-3	11.8	5.593	−6.446
K-19	L-3	14.9	4.161	−6.414
K-20	L-3	17.6	4.475	−6.034
L3-3	L-3	18.1	4.604	−6.750
L3-4	L-3	19.8	5.008	−6.748
L3-6-1	L-3	21.9	4.886	−7.504
L3-6-2	L-3	22.0	4.547	−6.533
L3-7	L-3	23.4	4.713	−5.969
L3-8	L-3	24.8	4.393	−5.022
K-22	L-3	25.1	4.797	−6.642
L3-9	L-3	25.7	5.488	−6.891
L3-10	L-3	27.2	5.563	−7.429
K-23	L-3	27.3	5.773	−7.510
L3-11	L-3	28.1	4.201	−6.664
L3-12	L-3	29.0	4.440	−8.001
K-24	L-3	29.6	4.802	−8.104
L3-13	L-3	30.9	4.021	−7.914
K-25	L-3	31.1	4.290	−8.150
L3-14	L-3	31.6	4.131	−8.108
K-26	L-3	32.4	3.971	−8.143
K-27-Yg-m	L-3	32.7	4.503	−7.887
L3-15	L-3	33.3	3.947	−7.767
L3-16	L-3	33.7	4.116	−8.291
L3-16.1	L-3	33.9	5.850	−6.803
K-28	L-3	34.0	2.864	−8.931
L3-17-1	L-3	34.2	4.834	−8.074
L3-17-2	L-3	34.2	5.030	−8.020
L3-17.1	L-3	34.8	5.784	−6.081
K-29	L-3	35.2	2.972	−7.850
L3-18.1	L-3	35.3	5.949	−6.125
L3-18.2	L-3	35.4	5.961	−6.185
K-30(dol)		35.5	1.968	−9.084
K-31(dol)		36.2	3.839	−5.621
K-32(dol)		69.4	4.973	−6.768
K-33(dol)		118.5	2.003	−4.649

values indicate that the Middle Permian shallow marine seawater became ^{13}C-enriched in the westernmost Paleo-Tethys. It is noteworthy because such high positive values of $\delta^{13}C_{carb}$ are not merely unique in the Permian rocks of the Tethyan domains (e.g., Korte et al., 2005) but also apparently higher than the average of Phanerozoic carbonates (e.g., Veizer et al., 1999).

All of the 3 limestones of the Brušane section biostratigraphically belong to the *Yabeina* (*syrtalis*) Zone that is correlated with the Capitanian at GSSP in West Texas or with the middle-upper part of Midian in Transcaucasia (Aljinović et al., 2008; Fig. 3). Thus the present data record the unique Capitanian event characterized by high positive $\delta^{13}C_{carb}$ values in western Paleo-Tethys. The stratigraphic duration of this high positive interval is not sufficiently constrained at the Brušane section, owing to the extensive dolostone development both above and beneath the informative black limestones. Nonetheless, the basal part of L-1 and the top of L-3 are characterized likewise by high positive values over +5.0‰, although both parts are in direct contact with massive dolostone. Thus the interval with high positive $\delta^{13}C_{carb}$ values over +5.0‰ may possibly extend farther downward and upward than currently examined.

5.2. The Kamura event in Paleo-Tethys

Extremely high positive $\delta^{13}C_{carb}$ values were rarely reported to date from the Permian shallow marine carbonates, in particular from the Guadalupian rocks (e.g., Veizer et al., 1999; Korte et al., 2005). As to the later half of the Permian, however, the $\delta^{13}C_{carb}$ values over +5.0‰ were recently reported from a mid-Panthalassan paleoatoll carbonates in Japan (Isozaki et al., 2007a,b; Fig. 5A). This interval with high $\delta^{13}C_{carb}$ values reaching +7.0‰ lasted at least for 3 million years of the early-middle Capitanian. In contrast, both the underlying Wordian and overlying Wuchiapingian rocks lack this unique signal (Isozaki et al., 2007b; Brand et al., 2009; Musashi et al., 2010); therefore, this remarkable phenomenon has been named the Kamura event with special emphasis on a unique oceanographic event that appeared in the Capitanian mid-superocean (Isozaki et al., 2007a).

The interval with the high positive $\delta^{13}C_{carb}$ values detected in the Upper Velebit Formation in central Croatia is apparently correlated with that of the Kamura event in mid-Panthalassa. This implies that the Kamura event occurred also in the Tethyan domain, or European Tethys that includes both Paleo-Tethys and Neo-Tethys. The Brušane section at the western end of equatorial Paleo-Tethys was located almost at the opposite side of the globe with respect to the Permian paleo-atoll complex in the middle of the superocean (Fig. 1). The depositional site of the paleo-atoll was paleomagnetically positioned at 12° South (Kirschvink and Isozaki, 2007), and also estimated at about 3000 km to the east of South China according to its subduction-related tectonic history (Isozaki and Ota, 2001; Ota and Isozaki, 2006).

Also in fossil content, the Brušane section in Croatia and the paleo-atoll section in Japan are intimately correlated with each other, as shown in Fig. 3. They share the same Tethyan fauna consisting of abundant large-tested fusulines (Verbeekinida), large bivalve (Alatochonchidae), rugose corals (Waagenophyllidae), and abundant algae (Kochansky-Devidé, 1965, 1978; Ota and Isozaki, 2006; Aljinović et al., 2008). In particular, the black limestone of the upper Velebit Formation (L-1 to L-3) all belong to the Capitanian *Yabeina syrtalis* Zone that is correlated with the *Yabeina globosa* Zone+ *Lepidolina multiseptata* Zone in eastern Paleo-Tethys (Fig. 3). *Lepidolina* was an endemic fusuline genus that was abundant in eastern Tethys but rare to absent in the western half. This biostratigraphical correlation between the Velebit Mtn. and the paleo-atoll unit in Japan supports the global context of the Kamura event.

Given that the Kamura event occurred globally, other contemporary sections in the rest of the world should have recorded similar signals. According to the compilation by Korte et al. (2005), most of the previously reported $\delta^{13}C_{carb}$ data of the Permian show moderately high positive values of +3 to +4‰ for the Guadalupian. Nonetheless, there are some fragmentary data sets that suggest the ubiquity of the Kamura event. For example, high positive $\delta^{13}C_{carb}$ values over +5‰

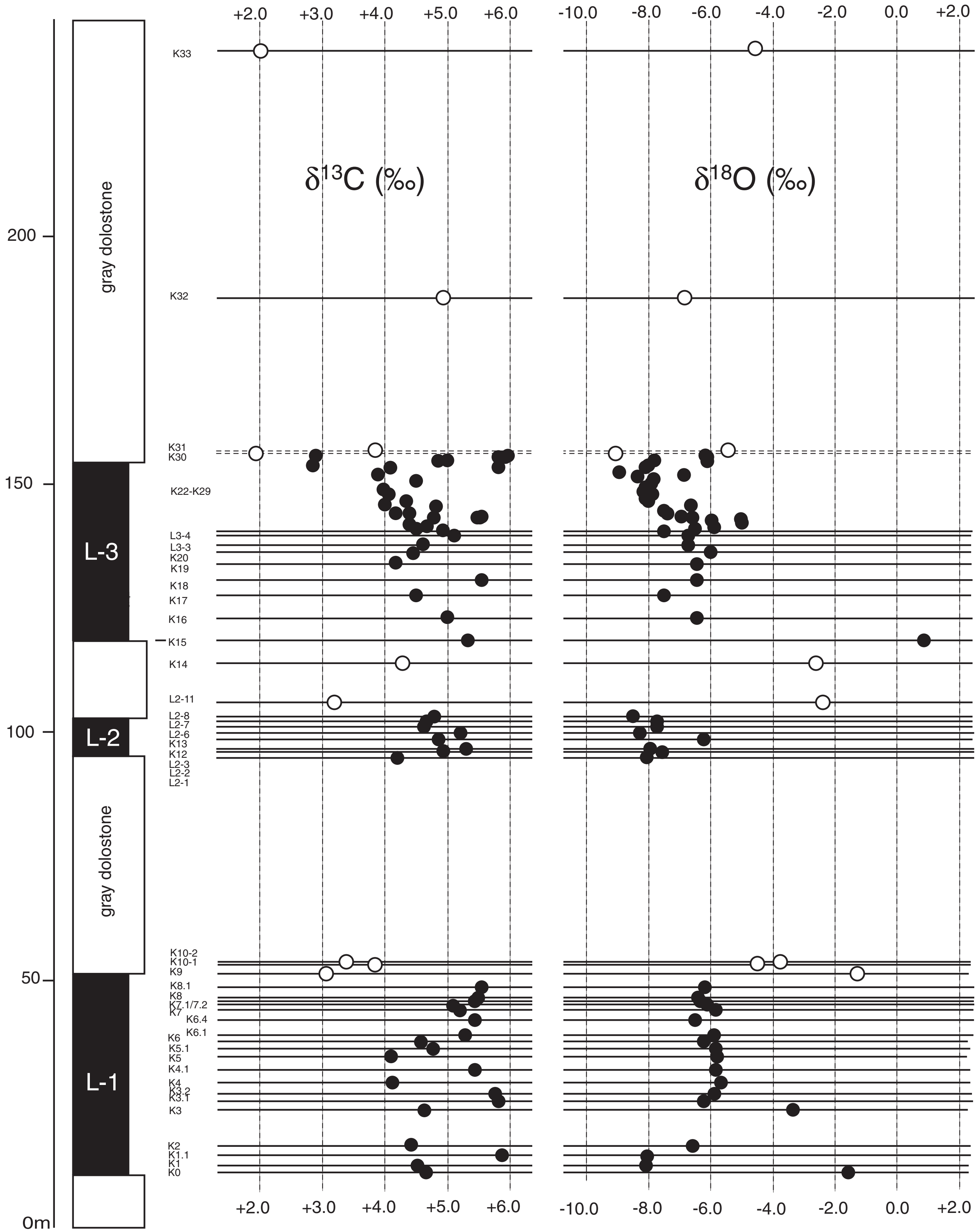

Fig. 4. Stable carbon and oxygen isotope stratigraphy of the Capitanian Velebit Formation in the Brušane section in central Croatia (samples from black limestone are shown by filled circle, whereas those of dolostone and dolomitic limestone by open circle). See Table 1 for raw measurements. Note the high positive $\delta^{13}C_{carb}$ values occur in all three Capitanian limestone units L-1, L-2, and L-3. In particular, the outer envelope on the higher values side stays over +5.0‰ throughout the studied section. In contrast, dolostones have relatively lighter $\delta^{13}C_{carb}$ values, probably reflecting the secondary diagenetic alteration. These data indicate that the upper Velebit Formation is characterized by the overall high positive $\delta^{13}C_{carb}$ values, and suggest its deposition under high primary productivity. This unique Capitanian chemostratigraphic interval first recognized in Paleo-Tethys is correlated with the Kamura event in mid-Panthalassa on the opposite side of the Earth from the Permian Velebit Mtn. of the Dinarides (Fig. 1).

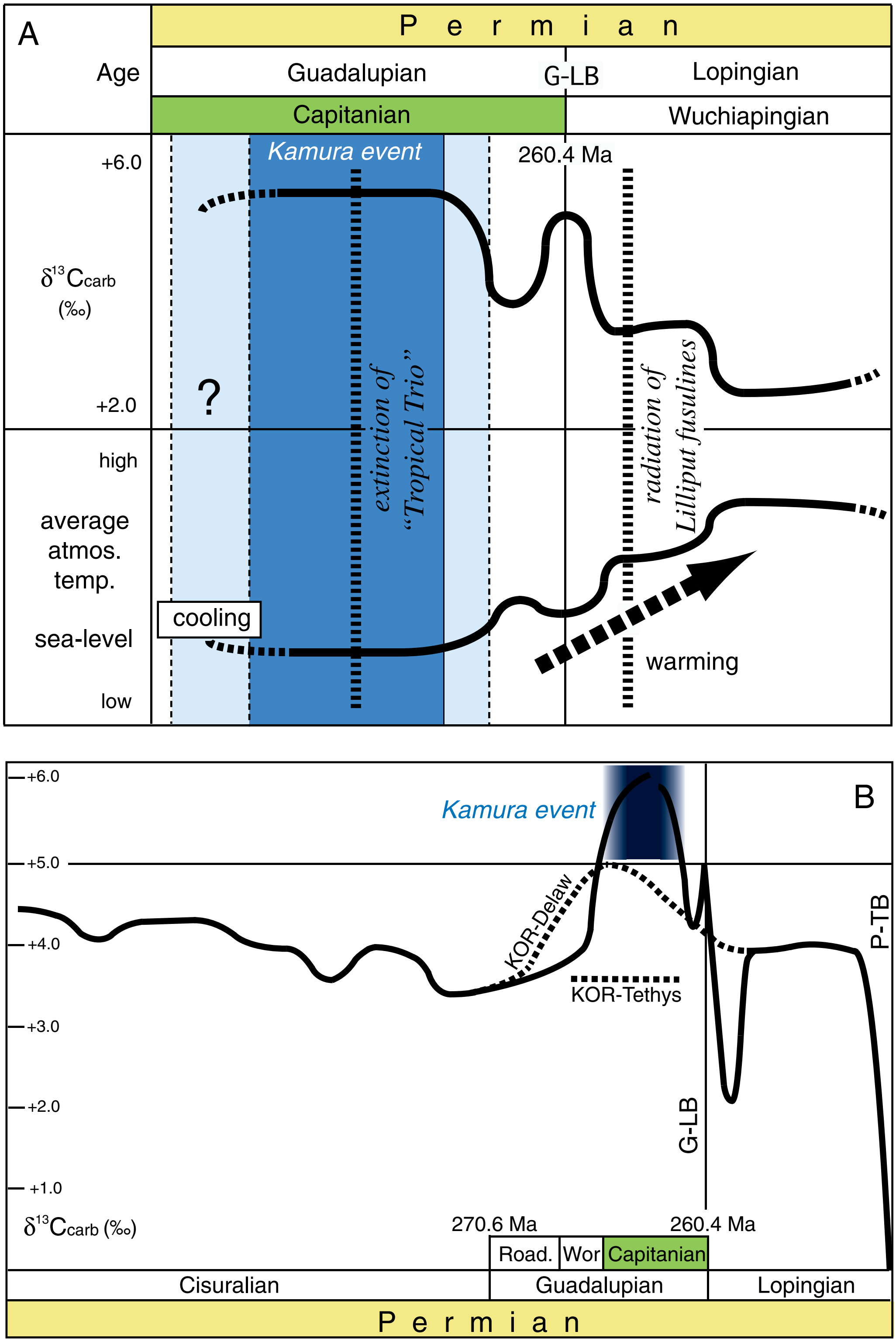

Fig. 5. Schematic diagram showing the late Guadalupian Kamura event with high positive $\delta^{13}C_{carb}$ values (modified from Isozaki et al., 2007b) (A), and the composite Permian secular curve of $\delta^{13}C_{carb}$ values modified from Korte et al. (2005) (B) with additional data by Isozaki et al. (2007a,b; this study). Road: Roadian, Wor: Wordian. Note that the Guadalupian large fusuline and bivalve fauna became extinct in the middle of the Kamura cooling event (Ota and Isozaki, 2006; Isozaki and Aljinović, 2009), whereas the post-extinction radiation of the Lopingian small fusulines started during the subsequent warming period (A). Korte et al. (2005) showed two possible trajectories (broken lines) for the Guadalupian secular change of $\delta^{13}C_{carb}$ values; the lower broken line (KOR-Tethys) for the Tethyan domain, the upper broken line (KOR-Delaw) for the Delaware basin in Texas (B). The Capitanian Kamura event recorded much higher positive $\delta^{13}C_{carb}$ values over +5.0‰ than both KOR-Delaw and KOR-Tethys for this interval. This common isotopic signal both in western Paleo-Tethys and mid-Panthalassa suggests that the world surface seawater has become extremely enriched in ^{13}C probably by high productivity and high burial of organic material (Isozaki et al., 2007b).

were sporadically reported from the Delaware basin in West Texas (Given and Lohman, 1985; Korte et al., 2005), East Greenland (Scholle et al., 1991), and West Spitsbergen (Gruszczynski et al., 1989; Mii et al., 1997). All these three areas were physiographically separated from Paleo-Tethys but connected to Panthalassa (Fig. 1). As to the Delaware basin, Korte et al. (2005) explained that the high positive anomaly may have represented a local phenomenon that occurred only within a restricted basin setting because less-restricted Tethyan data in general show relatively lower $\delta^{13}C_{carb}$ values less than +4.0‰. Although any direct record for mid-Panthalassan seawater was not available then, they concluded that the moderately high $\delta^{13}C_{carb}$ values around +4.0‰ may represent a global average for the Middle Permian seawater (broken line marked as KOR-Tethys in Fig. 5B).

The study on the paleo-atoll carbonates in Japan provided the first evidence for the high positive $\delta^{13}C_{carb}$ values for the Capitanian (Isozaki et al., 2007a, b; Fig. 5A) that are almost identical to the values previously reported from West Texas, Greenland and Spitsbergen (broken line marked as KOR-Delaw in Fig. 5B). As the paleo-atoll carbonates were deposited in the middle of the superocean, without any physiographical constraints from local basin geometry or from local flux of continental run-off, the isotope data likely reflect a general signature of surface water of the mid-superocean (Fig. 1). On the other hand, sediments deposited along continental margins adjacent to lands are usually prone to variable local factors. Supporting this viewpoint, Brand et al. (2009) recently pointed out that the C-isotope records from epeiric seas tend to have a large deviation from those of contemporary mid-oceanic and open shelf environments. In this regard, the Delaware basin was likely washed by the normal Panthalassan seawater rather than by local seawater of a restricted basin with unique isotopic composition as previously claimed. The approach by Korte et al. (2005) with keen selection of well-preserved brachiopod shells was fair and orthodox for monitoring precise isotopic signals of past seawater; however, this type of approach with strict selection of fossil specimens may sometime bring sampling bias for unchecked intervals without well-preserved fossils.

The above results suggest the ubiquity of the high positive C-isotope composition throughout the Capitanian Panthalassa. The present result from Croatia is particularly noteworthy because it represents the first dataset for the extremely high positive $\delta^{13}C_{carb}$ interval for the Capitanian in Paleo-Tethys, at least in its western part. As long as the above-listed three low-latitude areas are concerned, i.e., the western Paleo-Tethys, the Delaware basin on the western margin of Pangea facing eastern Panthalassa, and the paleo-atoll carbonates in mid-Panthalassa (Fig. 1), they shared the same C-isotope record of seawater. In addition, the data from high latitude domains in Greenland and Spitsbergen further confirm the homogeneous C-isotope composition of the global seawater. Consequently, the identical C-isotope composition on a global scale indicates that the world seawater was efficiently mixed during the Capitanian among the open Panthalassan ocean, basin-like embayment along Panthalassa, and the western dead-end of Paleo-Tethys (Fig. 1). Under the circumstances, therefore, the Kamura event appears to be a promising clue for the global chemostratigraphic correlation of the Middle Permian rocks, although its chronological range needs more refinement (Fig. 5).

5.3. High productivity

In general, extremely high positive $\delta^{13}C_{carb}$ values in surface seawater indicate high primary productivity in the ocean and burial rate into sediments (e.g., Kump and Arthur, 1999; Saltzman, 2005). As oceanic productivity is strongly controlled by nutrient availability, constant supply particularly of limiting elements, such as phosphorous and nitrogen, is necessary to maintain long-lasting high productivity. High riverine run-off, intense upwelling of deep-sea water, or the combination of the two, is likely needed to maintain major high productivity events. Saltzman (2005) emphasized the significance of P supply to drive high-positive excursion of $\delta^{13}C_{carb}$ values during the Paleozoic with anoxic deep-water.

The extremely high positive $\delta^{13}C_{carb}$ values of the Velebit Formation apparently indicate that the carbonate platform along western Paleo-Tethys recorded an unusual high productivity event during the Capitanian. This is in accordance with the black color of limestone with relatively high TOC (~0.9 wt%) and enriched fossil remains, particularly diversified algae (e.g. Herak and Kochansky-Devidé, 1960; Kochansky-Devidé and Herak, 1960). As the similar high positive $\delta^{13}C_{carb}$ value in the Capitanian was also detected in other parts of the world; i.e. low-latitude mid-Panthalassa, West Texas, East Greenland, and Spitsbergen, the Capitanian high productivity in surface seawater likely occurred on a global scale. Given that the Kamura event records a global high productivity episode, the following two points need to be explained; i.e., how to cause high productivity on a global scale, and how to maintain it for nearly 3 m.y. during the Capitanian.

In general, normal shallow marine environments in tropical seas are kept under oligotrophic conditions (e.g., Hallock, 1999). The Velebit Mtn. of the External Dinarides was located around the paleo-equator during the Permian (Fig. 1), and the occurrence of rich photosymbiotic fauna (fusulines, large bivalves, rugose corals) proves the general prevalence of oligotrophic conditions in shallow seas (Aljinović et al., 2008) as explained later. Nonetheless, the high positive $\delta^{13}C_{carb}$ values suggest that a unique high productivity event may have appeared in the shallow western Paleo-Tethys. A possible explanation for such a contradictory situation in the late Guadalupian is the temporary appearance of an unusual condition that increased nutrient supply across a threshold, above which the tropical oligotrophic environments as well as relevant animals were terminated. It is generally difficult to expect strong upwelling on the eastern side of continent, in particular, in the *cul-de-sac* of Paleo-Tethys on the east side of Pangea. A rapid increase in riverine flux may be a reasonable explanation for the “Kamura event” in the Velebit Mtn. Located next to the Permian northern Gondwana margin, the active rifting of Neo-Tethys on the south could have driven a local increase of nutrient flux from continental crust.

Such a local increase in riverine run-off, however, may not explain the entire Kamura event, in particular, the high productivity in the mid-superocean far away from any continental margin. Isolated from direct continental influence, oceanic upwelling of deep-sea water enriched in nutrients is inevitable to explain a high productivity in mid-ocean. The marginal basins in West Texas, E. Greenland, and Spitsbergen located on the western side of Pangea were likely influenced by coastal upwelling of deep-sea as well as the riverine run-off from western Pangea. In order to maintain a long-term high productivity, such as the Kamura event that lasted for 3 m.y., the combined effects of increased terreigenous flux and accelerated oceanic circulation appear necessary.

5.4. Late Guadalupian global cooling

The enhancement of oceanic circulation is generally driven by the surface cooling that makes a large temperature gradient between high-latitude and low-latitude regions. The appearance of global cooling in the Capitanian was recently proposed by Isozaki (2009a,b) on the basis of various lines of geological evidence summarized in Table 2; i.e. the high positive $\delta^{13}C_{carb}$ values (Isozaki et al., 2007b), the lowest sea-level of the Phanerozoic (Haq and Schutter, 2008), the migration of mid-latitude fauna into the tropical domain (Shen and Shi, 2002), and the die-off of some tropically-adapted fauna (Isozaki and Aljinović, 2009; Figs. 3 and 5). Saltzman (2005) explained how high positive $\delta^{13}C_{carb}$ values in seawater are driven during transient cooling in terms of the availability of essential nutrients. Brand et al. (2009) recently confirmed that the intervals with high positive $\delta^{13}C_{carb}$ values of 5.2–6.9‰ during the Paleozoic correspond to cool periods. The lowering of the global sea-level down to the Phanerozoic minimum was likely achieved by stabilizing large amounts of ice on land. Fielding et al. (2008) recently identified another cool interval in the late Middle Permian that was not previously recognized, although the cause of the Phanerozoic lowest sea-level in the late Middle

Table 2
List of geological lines of evidence for global cooling during the Capitanian

Category	Constraints	Driving mechanism	References
1. Stable C-isotope ratio	High $\delta^{13}C_{carb} > +5.0‰$	High productivity + high burial rate	Isozaki et al. (2007a,b)
2. Sea-level	The lowest in the Phanerozoic	On-land ice-stabilization	Haq and Schutter (2008)
3. Glaciation	Glacio-marine deposits, glendonite in E. Australia	Cooling in high latitude	Fielding et al. (2008)
4. Faunal migration	Escape of mid-latitude brachiopods to tropical domains	Temperature drop in mid-latitude	Shen and Shi (2002)
5. Extinction	Disappearance of the “tropical trio”	Temperature drop, eutrophication in low-latitude	Isozaki and Aljinović (2009)

Permian after the main Gondwana glaciation has not been sufficiently explained.

As to the fossil records, it is noteworthy that mid-latitude brachiopods made their first appearance in the tropical domain in the beginning of the Capitanian (Shen and Shi, 2002) because this implies their escape to relatively warm low-latitude refugia due to the appearance of cool climate. Also geologically significant is the extinction of the unique tropical-adapted fauna composed of large-tested fusulines, gigantic bivalves, and rugose corals (tropical trio by Isozaki and Aljinović, 2009) that occurred during the Kamura event (Isozaki et al., 2007a; Fig. 3). In general, modern shallow marine animals in tropical domains survive in oligotrophic conditions by employing special ecological strategies, particularly photosymbiosis (e.g., Brasier, 1995; Hallock, 1999). The above three groups of animals were pioneers of such photosymbiotic strategists, and they flourished and declined almost at the same time, even though they are considerably separated from each other in phylogenic lineages. The tropical trio disappeared almost simultaneously during the Kamura event in the mid-Panthalassa (Isozaki et al., 2007a,b; Figs. 3 and 5). At the Brušane section, the top of the black limestone (L-3) recorded both the abundant occurrence of large-tested fusulines (*Yabeina*) and high positive $\delta^{13}C_{carb}$ values (Fig. 4), although both the terminal horizon of the Kamura event and the extinction horizon of the tropical trio were not identified because these were concealed probably within the overlying massive dolostone.

The later half of the Permian was fundamentally characterized by the overall global warming trend after the severe Gondwana glaciation during the Late Carboniferous to Early Permian (e.g., Fielding et al., 2008). The appearance of a temporary cool climate in the Capitanian might have somehow destroyed the comfortable habitat of the Guadalupian tropical trio that was fostered under warm-water environments. In particular, the lowering of sea surface temperature was likely fatal for the survival of warm-water loving animals and also inevitable in accelerating ocean circulation with excess nutrient supply from deep-sea to ocean surface and resultant high productivity. In addition to the low-temperature damage, the tropical creatures adapted to the pre-existing oligotrophic conditions were naturally vulnerable to entrophication. The Capitanian Kamura high-productivity-cooling event might possibly have driven some Guadalupian marine creatures, in particular those adapted too well to tropical oligotrophic environments, toward extinction through the temperature drop and eutrophication.

As to the cause of the cooling in the late Guadalupian, two possible triggers have been suggested; volcanic cooling by the activation of a large igneous province (e.g., Courtillot, 1999) and geomagnetic cooling with respect to galactic cosmic radiation (Isozaki, 2009a). One of the well-known large areas of volcanism activated around the G–LB timing is at Emeishan (flood basalt derived from a mantle plume) in South China that has been often nominated as a cause of the G–LB extinction (e.g., Ali et al., 2002; Zhou et al., 2002; Wignall et al., 2009). Its eruption timing, however, appears too late to have been responsible for the early Capitanian onset of the Kamura cooling event, gradual biodiversity decline (Clapham et al., 2009), and equator-bound migration of the mid-latitude fauna (Shen and Shi, 2002) (Table 2), and also its size was likely too small to cause the global cooling that affected the Guadalupian biota. Thus the Emeishan Trap alone may not explain the environmental change in the Capitanian and/or the end-Guadalupian extinction. By focusing on the pattern of geomagnetic polarity change during the Permian, Isozaki (2009b) further speculated that both mechanisms, i.e. geomagnetic cooling and volcanic cooling, became activated in succession under the control of the same mantle super-plume activity that initially split the eastern part of Pangea in the late Middle Permian. The volcanic warming might have followed after the end-Guadalupian initial volcanic cooling that faded away in the early Lopingian. Refer to the above references for further details, as the cause of the cooling was not at the main focus of this article.

6. Conclusions

Our chemostratigraphic analysis using stable carbon isotope ratios confirms that the Capitanian limestone deposited in the western end of Paleo-Tethys records a unique interval characterized by high positive $\delta^{13}C_{carb}$ values over $+5.0‰$. This unique signal in Croatia is chemostratigraphically correlated with the Kamura event detected in mid-Panthalassan paleo-atoll carbonates in Japan. As these two Capitanian sections formed both in low-latitude domains at almost the opposite sides of the globe, their correlation suggests a global development of the Kamura event and its utility in global chemostratigraphic correlation. The high positive $\delta^{13}C_{carb}$ values likely indicate high primary productivity and burial rate into sediments both in Panthalassa and Paleo-Tethys. Global cooling was a likely cause of the Kamura event and the associated low-temperature/eutrophication might have driven the extinction of some low-latitude fauna adapted to tropical climate.

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