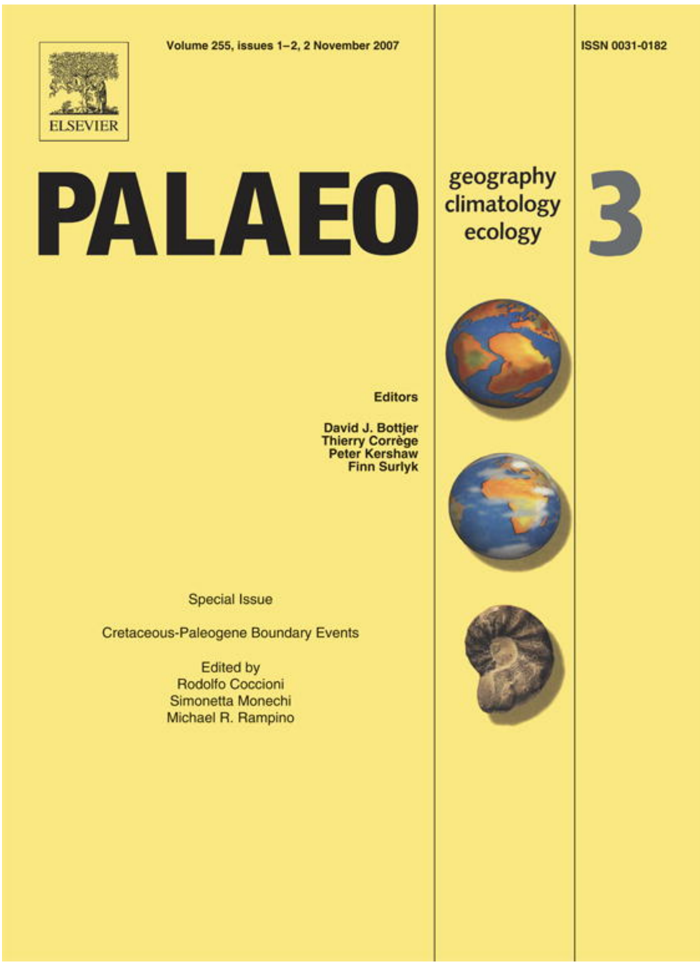
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Peritidal sedimentary depositional facies and carbon isotope variation across K/T boundary carbonates from NW Adriatic platform

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Abstract

The K/T boundary in the Karst region (Italy and Slovenia) is well documented in correspondence to shallow water limestones. Its evidence is usually related to palaeontological data (disappearance of Cretaceous taxa and subsequent appearance of Tertiary ones), palaeomagnetism (Ch 29r) iridium anomaly and negative shift of $\delta^{13}C$.

In Italy, the Padriciano section highlights the K/T boundary included in the basal breccia of a peritidal cycle. Recent investigations brought to light a short well exposed new stratigraphic sequence containing the K/T boundary, 100 m east of Padriciano, as demonstrated by lithological, palaeontological and new isotopic data. The recording of a new peritidal setting denotes stressed environmental conditions. The findings of the biota mostly correspond to the lagoonal limestones of the peritidal cycle. It consists of small opportunistic thin shelled foraminifers, ostracods and gastropods. At Padriciano, the environmental stability occurred after episodes of strong fresh water influence. The intraclasts, oncolites and stromatolites have been observed in the Padriciano section. The broken shell fragments, algae and foraminifera have been found associated with fenestral fabric. These features indicate deposition in a shallow marine (intertidal to supratidal) environment. Algal boundstones and microbial (stromatolitic) laminae, crenulated domal laminae and crenulated conical laminae have been studied in petrographic sections for microstructures. The K/T boundary section has been analysed for the carbon and oxygen isotopic ratios. The $\delta^{13}C$ values range from −3.62 to −10.01‰ (V-PDB) and the $\delta^{18}O$ values range from −3.85 to −5.47‰ (V-PDB). This extreme depletion in the $\delta^{13}C$ record has already been reported from other K/T boundary sections both in the Padriciano area (Italy) and in Slovenia (Dolenja Vas sections) and may be related to global climate change but also to local environmental changes occurring in the NW Adriatic Platform.

Keywords: Cretaceous–Tertiary boundary; Peritidal; Carbon isotopes; Adriatic Platform; Padriciano; Extraterrestrial impact; Mass extinction; N Italy

1. Introduction

The extraterrestrial bolide impact at the Cretaceous–Tertiary boundary is one of the most widely accepted reasons for the catastrophic mass extinction on Earth about 65 million years ago (Ganapathy, 1980; Alvarez

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et al., 1980; Montanari et al., 1983; Alvarez et al., 1984a,b; Alvarez, 1987). The bolide impact theory is strongly supported by the impact derived spherules and the rich concentration of the rare earth element iridium and other platinum group elements in the boundary clay layer from Yucatan Peninsula (Mexico), Sugarite section in New Mexico (USA), Gubbio and Padriciano sections of Italy, Dolenja Vas section of Slovenia and Um Sohrynkew section of NE Himalaya, India (Izett, 1990; Hansen et al., 1995; Bralower et al., 1998; Gregorič et al., 1998; Bhandari, 1999; Tewari, 2004). The mass extinction of planktonic foraminifera at the K/T boundary is related to this impact (Smit, 1982; Molina et al., 1996). The benthic foraminifera show reorganisation and resulted from the drop in biotic productivity after the asteroid impact at the end Cretaceous (Alegret et al., 2002). The sedimentological and geochemical study of the carbonate rocks across the K/T boundary in the Karst area of Italy (Padriciano) and the sections of Slovenia (Dolenja Vas and Sopada) in the NW Adriatic platform also support the impact related extinction (Drobne et al., 1988; Drobne et al., 1989; Ogorelec et al., 1995; Pugliese et al., 1995; Hansen et al., 1995; Brazzatti et al., 1996; Drobne et al., 1996; Palinkaš et al., 1996). Mass oceanic extinction was world wide and about 90% of the planktonic foraminifera perished. This extinction event was also linked with the major change in the global carbon cycle (Beerling et al., 2001). Stable carbon isotope studies of planktonic foraminifera show a δ^{13}C negative excursion following the K/T boundary mass extinction (Boersma and Shackleton, 1981 in Beerling et al., 2001 and the references therein). The depletion of δ^{13}C values indicates a drop in marine primary productivity following mass extinction. The decrease in the carbonate carbon and organic matter δ^{13}C at the K/T boundary is also interpreted as being related to global climatic cooling and mass extinction (Gartner and James, 1979; Schimmelman and De Nero, 1984; Magaritz, 1989; Mayers, 1992).

The main aim of this paper is to establish a carbon isotope stratigraphy and depositional environmental changes across the K/T boundary in the NW Adriatic Platform. Focusing, in particular, on the Italian territory, this paper studies Padriciano 1 and 2 sections outcrop, already called Padriciano West and East by Pugliese et al. (2000), respectively. Here, we report new stable isotope measurements (δ^{13}C and δ^{18}O) and detailed micropalentological and palaeoenvironmental results from the Padriciano 2 section across the K/T boundary. Taking into account the biostratigraphic data of these sections (Pugliese et al., 1995, 2000), the new data will be compared to other sections in the NW Adriatic Platform previously published by Ogorelec et al. (1995).

2. The K/T boundary sections in NW Adriatic Platform

The Karst region (North Italy with the Trieste area and SW Slovenia) is part of the NW Adriatic platform and is characterised by Cretaceous–Tertiary (K/T) boundary peritidal carbonate deposits (Fig. 1). In Italy, the thickest seque7nce is located at Padriciano. There, the K/T boundary is well documented in the peritidal environments of two already signalled sections (Padriciano east and west sections of Pugliese et al., 2000) and in at least two other unpublished sections east of Padriciano. These environments are characterised by unstable conditions with frequent peritidal (subtidal to supratidal) environmental fluctuations (Pugliese et al., 1995, 2000).

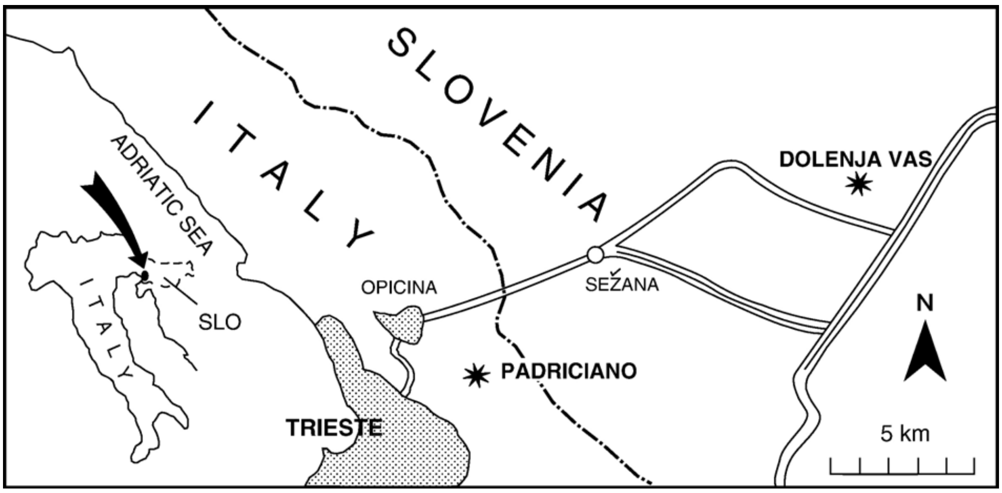

Fig. 1. Map showing the location of the main investigated localities.

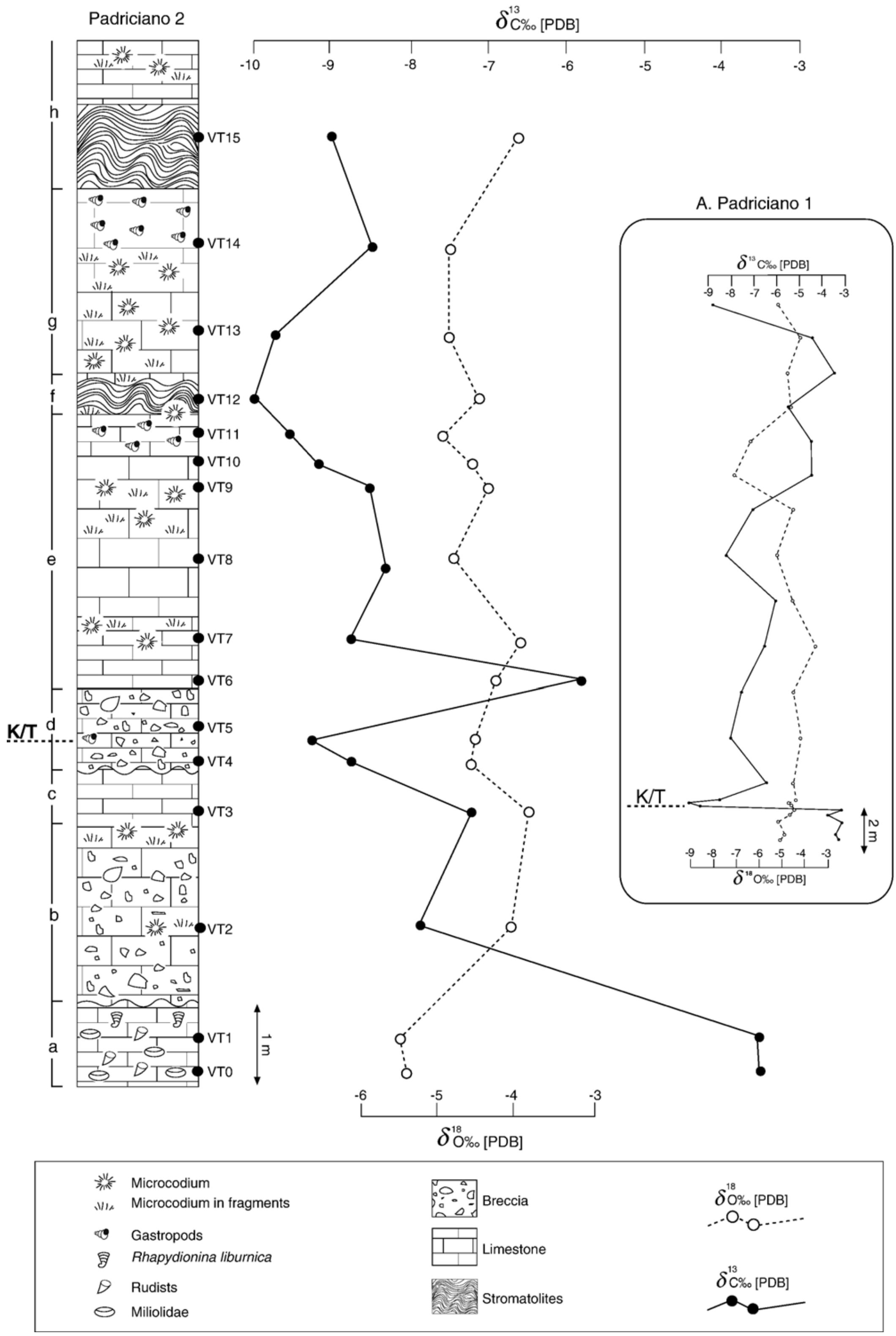

Fig. 2. Stratigraphic column of Padriciano 2 section with δC^{13} and δO^{18}data. Box A reports geochemical data across K/T boundary in the Padriciano 1 section (after Ogorelec et al., 1995, modified).

The peritidal sequence at Padriciano shows well developed Maastrichtian breccia, dark limestone with rudist shell fragments and foraminifera, such as Miliolidae, *Rhaphydionina liburnica* (Stache) and *Fleuryana adriatica* De Castro, Drobne et Gušiæ (De Castro et al., 1994). The light grey limestone with breccia and

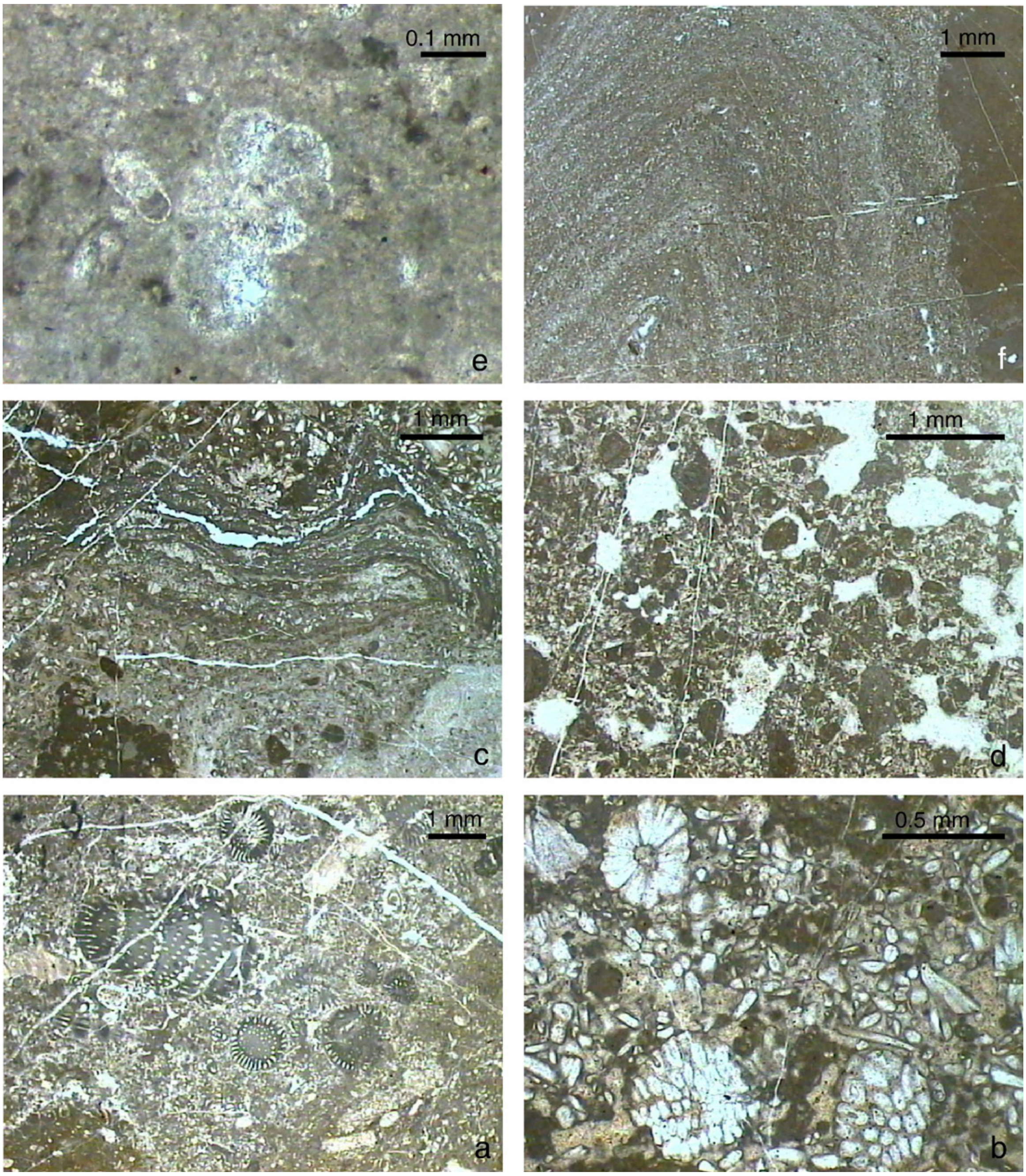

Fig. 3. a — (sample Vt1), wackestone with *Rhapydionina liburnica*; b — (sample Vt2), packstone with *Microcodium*; c — (sample Vt2) packstone with stromatolitic laminae; d — (sample Vt4) breccia with *Microcodium* fragments and intraclasts; e — (sample Vt8) wackestone with *Bangiana hanseni*; f — (sample Vt12) stromatolitic laminae showing stratified and conical microstructure.

Microcodium overlies the dark limestone. The K/T boundary lies within the breccia interval. The thick sequence of Danian grey limestone is overlain by stromatolitic limestone with *Microcodium*. The brown limestone, with gastropod fragments and *Microcodium* in turn, is overlain by grey stromatolitic limestone capped or penetrated by *Microcodium*. Recordings of the low diversity biota include ostracods, gastropods and dasycladacean algae (Barattolo, 1998). Other K/T boundaries are well exposed in the Dolenja Vas road section and the adjoining forest sections in Slovenia. These present thin breccia layers and short peritidal episodes followed by open marine depositional environmental conditions with respect to the Padriciano sections (see: Ogorelec et al., 2007-this volume). These latter sequences have been studied in detail across the K/T boundary to highlight sedimentary facies, biota, petrography and stable carbon and oxygen isotope variations (Ogorelec et al., 1995) and paleomagnetism (Marton et al., 1995).

All these data suggest that the above mentioned sections (Padriciano 1, Padriciano 2, Dolenja Vas West and East), together with those at Čebulovica and Sopada, may belong to the Biosedimentary zone 2, as reported by Drobne (2000, 2003) and Drobne et al. (in press) in their palaeobiogeographic studies. In this zone, the K/T transition on the carbonate platform records a generally longer hiatus between Upper Cretaceous and Paleogene limestone than the biosedimentary zones 3 and 4.

3. Microfacies and palaeoenvironment

3.1. Padriciano sections

As previously mentioned, two sections have been studied at Padriciano. Padriciano 1 has already been described by Pugliese et al. (1995) and Brazzatti et al. (1996) from Maastrichtian to Ilerdian beds. Padriciano 2 has been briefly described by Pugliese et al. (2000) and Tewari et al. (2004) from just below the K/T up to the first meters of lower Danian. Brief descriptions of these sections across the K/T boundary are reported below.

Padriciano 1: below the K/T boundary, four meters of Maastrichtian grey and brown-grey limestones have been measured. They yield the last Cretaceous taxa represented by rudists (*Bournonia* spp. and *Apricardia* sp.) and a rich microfossil content constituted by the foraminifers *Rhapydionina liburnica* (Stache), *Fleuryana adriatica* De Castro, Drobne and Gušiæ, and *Cuneolina ketini* Inan (see Caffau et al., 1998), etc. These limestones indicate subtidal lagoon environments, which show high hydrodynamic episodes (level of displaced rudists) and upwards a freshwater influence (characean girogonites).

Above these limestones, three shallowing episodes occur with a total thickness of 2.40 m. The first episode consists of i) a breccia with subrounded bioclasts and subordinate mm–cm clasts in a bioclastic matrix with the above mentioned last Cretaceous foraminifers, ii) a thin subtidal muddy layer capped by an erosional surface. The second episode is characterised by a breccia with rounded mm–cm muddy clasts overlain by wackestone–packstones with *Microcodium*. The third episode presents a breccia with clasts derived from the underlying level in a muddy matrix, capped by supratidal stromatolites. The K/T boundary occurs within a breccia layer of the second episode, as demonstrated by geochemical evidence (Ir-anomaly, negative shift of $\delta^{13}C$), palaeomagnetism data (Ch 29r) and disappearance of Cretaceous taxa.

Above the K/T boundary, numerous peritidal cycles are present. Within the lagoon limestones of these cycles, some Danian taxa appear characterising the SBZ 1 zone (*Bangiana hanseni* n.gen.n.sp., ex *Protelphidium*, Drobne et al., 1996).

Padriciano 2: a 14 m thick section has been measured across the K/T boundary, the lower 6 m of which are included in the Maastrichtian below the K/ T boundary (Fig. 2). Some units can be recognised:

a – (samples VT0–VT1): the lowermost one meter thick light grey bioclastic limestone is characterised by rudist shells, foraminifera such as Miliolidae and *Rhapydionina liburnica* (Stache), and ostracods (Fig. 3a). The microfacies identified are biomicrite (wackestone and packstone). This facies is deposited in a peritidal (restricted platform) environment.

b – (sample VT2): above an erosional surface, the overlying 2m thick sequence is mainly a breccia limestone with foraminifera Miliolidae and *Microcodium* (Fig. 3b). *Microcodium* is also found associated with stromatolitic laminae (Fig. 3c) and ostracods. This is a pelbiomicrite (packstone) microfacies.

c – (sample VT3): the 1m thick limestone just below the K/T boundary is light to dark grey in colour and predominantly breccia with gastropod shell fragments, foraminifera Miliolidae, *Microcodium* and ostracods. The intraclasts and fenestral fabric are well developed. The fenestral fabric is associated with *Microcodium* and recrystallization has obliterated the original fabric. Rare foraminifera (Discorbidae) have appeared at the top of the limestone.

d – (samples VT4–VT5): above an erosional surface the K/T boundary is characterised by 1m thick layer of intraformational breccia representing a peritidal depositional environment. The breccia varies in size from mm to a few cm. The breccia lithoclasts also contain small foraminifera such as Discorbidae and Miliolidae. The microfacies is biomicrite with *Microcodium* fragments (Fig. 3d). The breccia indicates an immersion phase at the K/T boundary time interval (Ogorelec et al., 1995).

e – (samples VT6–VT11): a 2m thick Danian limestone light grey in colour just above the K/ T boundary is characterised by foraminiferal assemblage (*Bangiana hanseni*, Fig. 3e) together with *Microcodium*, ostracods, characean girogonites, rare *Aeolisaccus barattoloi* De Castro, and gastropod fragments. Fenestral fabric and large well sorted clasts are also observed. The microfacies of the limestone is pelbiomicrite (packstone) and wackestone. This facies indicates a lagoonal environment.

f – (sample VT12): about 50cm thick stromatolitic limestone overlies this limestone and is characterised by *Microcodium*. In thin section, the stromatolitic laminae are stratified and conical in microstructure (Fig. 3f). Stromatolite forming photosynthetic microbiota (Cyanobacteria) must have been present in the intertidal–lagoonal facies.

g – (samples VT13–VT14): the stromatolitic limestone is followed by 3m thick brown and grey limestone with *Microcodium*, gastropod fragments and intraclasts. The limestone shows diagenetic changes and secondary veins are present. The one meter thick limestone contains thin bands of stratified stromatolites associated with *Microcodium* and Miliolidae. The microstructure of the stromatolitic laminae shows fragments of *Microcodium* within stromatolitic laminae.

h – (sample VT15): the top one meter of the measured section is a dark grey limestone with *Aeolisaccus barattoloi*, Discorbidae and *Microcodium*, and represents biomicrite microfacies. Moreover, frequent reappearences of *Microcodium* can reflect short stages of paleosol formation (Košir, 2004).

3.2. The Dolenja Vas section

In the Dolenja Vas section the K/T boundary is well exposed along the road section. The Maastrichtian limestone is deposited in a shallow subtidal environment. The microfacies are biomicrite and pelbiomicrite (wackestone and packstone) with *Rhapydionina liburnica* and *Apricardia* rudists (Drobne et al., 1996). The K/T boundary is characterised by a 20 cm thick layer of intraformational plastic breccia similar to that of Padriciano and represents a supratidal depositional environment with a short lasting emersion phase (Ogorelec et al., 1995; Hansen et al., 1995). The limestone of Lower Danian age is characterised by foraminifera (*Bangiana hanseni*, miliolids and discorbids), dasycladal algae and intercalations with *Microcodium* overgrowths (Drobne et al., 1988, pl. 4, 5). Some thin stromatolitic layers can also be observed.

The isotopic composition of the K/T limestone interval of the Dolenja vas section is shown in a paper by Ogorelec et al. (2007-this volume).

4. Carbon and oxygen isotope excursions across K/T boundary in the Adriatic Platform

The carbon and oxygen isotope analyses obtained from 16 whole rock carbonate samples, collected across the K/T boundary in the Padriciano 2 section, are shown in Fig. 2. From the base to the top of the studied carbonate sequence both carbon and oxygen isotope compositions exhibit negative values. $\delta^{13}C$ and $\delta^{18}O$ values range from −3.62 to −10.01‰ (V-PDB) and from −3.85 to −5.47‰ (V-PDB) respectively. Both the Maastrichtian limestone with rudist shells and Miliolidae at the base (sample number VT0) and the limestone with *Rhapydionina* (VT1) show similar and less negative $\delta^{13}C$ values. There is a drastic drop in the carbon isotope values in the light grey limestone with breccia and *Microcodium* (VT2 and VT3). The overlying grey limestone, with breccia and gastropod (VT4), shows a further depletion of its $\delta^{13}C$ value, and at the Maastrichtian–Danian boundary (VT5), a $\delta^{13}C$ value of −9.20‰ is obtained, suggesting that the K/T boundary occurs in the interval between VT4 and VT5. There is a drastic change toward less negative carbon isotope values of the first Danian limestone (VT6). The overlying limestones (from VT7 to VT15) show again more negative and more homogeneous carbon isotope values, which are decreasing slightly, toward the top of the sequence. The second lightest carbon isotope value (−10.01‰) occurs in correspondence to the stromatolitic limestone with *Microcodium* (VT 12).

Apart from the first two samples (VT0 and VT1), the oxygen isotope values show a lower variability, increasing slightly, toward the top of the sequence.

5. K/T boundary sections, iridium enrichment and extraterrestrial impact microspherules

Iridium (Ir) is abundantly found in meteorites and is a rare earth element (REE). Ir is also found in the mantle of the earth in low concentration. Abundance of Ir in the K/T boundary clay layer has been recorded from Mexico, North America, Europe and India.

The high iridium concentration at the K/T boundary is attributed to meteoritic or single bolide impact on Earth which caused mass extinction. This boundary clay layer, rich in Ir, has world wide significance.

The Um Sohryngkew River section of NE Himalaya, India exposes the K/T boundary section in clastic or carbonate facies characterised by nannoplankton fossils (Garg and Jain, 1995). The foraminiferal break and Ir anomaly has also been recorded from this section (Pandey, 1990; Bhandari, 1991). According to Bhandari (1991) the Um Sohryngkew river section in Meghalaya, NE Himalaya contains a strong and narrow peak of iridium concentration (12.1 ng /g) superimposed on a broad and mild band (Ir = 0.2 ng/g). The iridium is enriched by a factor of about 10 in the broad band and by a factor of about 500 in the sharp peak above the Cretaceous shales. The level of iridium anomaly in the Meghalaya section is similar to that found elsewhere in the world. Negi et al. (1993) reported a bolide impact related to the K/T boundary near Bombay (Mumbai) offshore. Bhandari (1991, 1999) has concluded that Deccan volcanism contributed a negligible amount to the global iridium inventory at K/T boundary. Deccan volcanism was not triggered by bolide impacts as suggested by Alt et al. (1988). The Deccan volcanism predates as well as post dates the K/T boundary event.

The other K/T boundary sections are well exposed on the east coast of India (Pondicherry and Thiruchirapalli) but the sequences have unconformity at the boundary.

The highest values of iridium have been recorded from Stevns Klint in Denmark which is around 185 ng/g. Multiple iridium layers in Gubbio sections of Italy have been recorded but there is no evidence of multiple impacts in deep sea sediments. Hansen et al. (1995) reported a higher value (5.8 ppb) of iridium from the K/T boundary breccia in Dolenja Vas W section of Slovenia.

K/T boundary glassy microspherules have been reported from different localities in the world and are believed to have been produced by the impact of a large asteroid in an ocean basin at the end of the Cretaceous period (Montanari et al., 1983). These microspherules have been reported from northern Italy, Spain, Tunisia and the Central Pacific (Gregorič et al., 1998). Gregorič et al. (1998) recorded unaltered glassy microspherules from the late Maastrichtian–Palaeocene breccia from the Padriciano section. Unaltered glassy microspherules are not very common in the old sediments and are interpreted as microtektites of extraterrestrial origin. A palaeokarst surface and layer containing glassy microspherules characterise the breccia interval. The spherules are found in the fractures of the breccia at the K/T boundary. The Sr-isotopic ratio of the Padriciano bauxite which contains microtektites reflects the sea water Sr-spike value characteristic of the K/T boundary (Gregorič et al., 1998). The C-isotope values (present work) also strongly support the K/ T boundary within the breccia interval (Fig. 2).

6. Discussion and conclusions

Drobne and Ogorelec with collaborators (1988, 1989) were the first to define the K/T boundary on the carbonate platform of the NW Adria plate, in the Karst region of Slovenia. The main criteria used for defining the K/T boundary was the biotic events with disappearance of Cretaceous taxa and appearance of Tertiary ones, palaeomagnetic identification of Ch 29r, iridium anomaly and strong negative shift in the carbon isotope values across the K/T boundary (Marton et al., 1995; Hansen et al., 1995; Ogorelec et al., 1995; Hansen and Toft, 1996; Palinkaš et al., 1996). The same criteria have been used in the Trieste Karst (Pugliese et al., 1995, 2000) to support the presence of the K/T boundary. Moreover, the finding of glassy microspherules (microtekites) at the top of the Maastrichtian breccia in an outcrop near Padriciano (Gregorič et al., 1998) may be further evidence of the presence of this boundary.

The Cretaceous–Tertiary boundary sections in Padriciano are characterised by several peritidal cycles such as deposition of basal breccia, lagoonal limestone, stromatolitic limestone and fenestral fabric (birds eye structures), *Microcodium* occurrence, etc. (Pugliese et al., 1995, 2000; Tewari et al., 2004). The uppermost Maastrichtian beds contain the last rudists (*Bournonia* and *Apricardia* specimens) and foraminifera such as *Rhapydionina liburnica* and *Fleuyriana adriatica* and *Cuneolina ketini* Inan (Caffau et al., 1998). In the shallow carbonate platform the K/T boundary lies in the basal peritidal cycle also in the new eastern section of Padriciano 2 (present work). The Maastrichtian–Danian transition has been established on the basis of characteristic microfossils (foraminifera) from Padriciano of Italy and Dolenja Vas sections of Slovenia in the north western Adriatic carbonate platform (Pugliese and Drobne, 1995; Pugliese et al., 1995, 2000, Tewari et al., 2004, Barattolo et al., 2005).

The K/T boundary extraterrestrial impact crisis affected several foraminifera and rudist taxa. The opportunistic and r-strategist foraminifera (small *Miliolidae, Bangiana hanseni*) appeared during Danian (SBZ 1) as demonstrated by Pugliese et al. (1995, 2000). The stressed and peritidal conditions were stabilised into the lagoonal limestone of the peritidal environment.

The negative carbon and oxygen isotope values obtained from the studied sequence suggest a strong influence of fresh water, characterized by negative $\delta^{18}O$ values, with the incorporation of carbon of terrestrial organic origin, which presents highly negative $\delta^{13}C$ values. The strong influence of fresh water is also in agreement with the microfacies and biota evidence indicating a deposition in shallow marine environment (intertidal to supratidal). The shift toward negative $\delta^{13}C$ values at the K/T boundary is in agreement with the pattern observed in other parts of the world (i.e. Hsü et al., 1982; Zachos et al., 1989). These negative carbon isotope excursions in marine carbonates, implying a global perturbation of the carbon cycle, that produces a decrease in the primary productivity (Zachos and Arthur, 1986; Magaritz, 1989), have been related to global climate changes caused by an impact of an extraterrestrial body (Alvarez et al., 1980).

One could argue that the negative $\delta^{18}O$ and $\delta^{13}C$ values could be affected by diagenetic alterations which normally alter the original signals, causing a negativization and a positive co-variance of both isotopic ratios. At Padriciano the $\delta^{18}O/\delta^{13}C$ plot show only a low correlation among the isotopic data ($r^2=0.2$) when considering the sample numbers from VT2 to VT15 and a negative correlation when considering all the data. Obviously, we cannot exclude that the $\delta^{18}O$ could have been shifted toward lower values due to interaction with isotopically light meteoric water or equilibration at higher temperatures during burial, but we are confident in the preservation of at least the primary nature of the carbon isotopic record. In fact, diagenetic re-crystallization of carbonates is occurring in a system with a low water/rock ratio for carbon, and a high ratio for oxygen (Veizer et al., 1999). Moreover, the fact that similar trends and values of $\delta^{13}C$ are observed in other sections of the NW Adriatic Platform gives us confidence in our interpretation. The isotopic data obtained from the Padriciano 2 sequence are in perfect agreement with another section studied in the same area by Dolenec in Ogorelec et al. (1995), who reported an extreme depletion of $\delta^{13}C$ up to −9.80‰ at the K/T transition. These authors suggested a strong influence of light terrestrial carbon in the sedimentary basin at the time of this transition. A $\delta^{13}C$ value of −7.15‰ is reported for the Sopada section in Slovenia by Ogorelec et al. (1995) at the K/T boundary and values around −8‰ are observed in different sections at Dolenja Vas in Slovenia (Dolenec et al., 1995; Ogorelec et al., 1995; Drobne et al., 1996).

A shift of 1–2‰ toward lighter $\delta^{13}C$ values is usually reported for other K/T boundary sections in marine carbonates in different parts of the world. Therefore, the extreme depletion in carbon isotope values observed in these peritidal sequences might suggest that this is a regional pattern in the NW Adriatic Platform. All the stratigraphic sequence at Padriciano (also below and above the K/T transition), showing the lightest carbon isotope values when compared to the Slovenian ones (Sopada and Dolenja Vas), suggest a more restricted shallow depositional environment for Padriciano than for Dolenja Vas and Sopada. This is in agreement to what is observed in the biota composition, which is more marine in Dolenja Vas than the Padriciano area. Conversely, as reported by Caffau et al. (1998), the Padriciano section yields characean girogonites, which may record a fresh water influence, in a level of limestones capping the upper Maastrichtian sequence. This situation is repeated in the Čebulovica section, suggesting that the Padriciano and Čebulovica sections are lying in the same paleogeographic direction (Ogorelec et al., 2001).

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