GLASS SPHERULES IN UPPER EOCENE FLYSCH OF CROATIAN ADRIATIC - EVIDENCE OF AN IMPACT INTO CARBONATE TARGET?

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ABSTRACT

Glass spherules occur at 7 levels in Late Eocene flysch marls of Central Dalmatian Basin (Croatian Eastern Adriatic), which are exposed in hinterland of the city of Solin. The spherules occur at one level in *Globigerinatheka semiinvoluta* zone, and in six levels of *Globigerinatheka index* zone, and their stratigraphic spacing ranges from 1,5 m to 93,3 m. The best studied, and with most spherules recovered, is a composite turbidite 2-7, which is youngest in the sequence. It comprises impact-generated debris in its marl part, which is represented by perfectly clear (sometimes slightly dimmed) glass spherules 91 to 530 μ across; teardrop transparent microtektites 1225 μ long, and fragments of vesicular glass 450 to 1000 μ across. Some spherules and microtektites comprise small bubbles with diameter up to 41 μ. Chemical composition of the spherules, poor in SiO_2 and relatively rich in CaO and MgO indicates possible carbonate target.

1. INTRODUCTION

The hypothesis on multiple impacts around the Eocene / Oligocene boundary [1, 2, 3, 4, 5, 6, 7] triggered continuous lively discussions in impact community. The number of Eocene impacts is a very controversial issue [8, 9], and ranges from 2 [9, 10] to >6 [5]. The cited evidence of impacts were horizons with microtektites and spherules, the latter associated also with an Ir-anomaly. The microtektites horizon occurs in the upper part of the *Globigeraspis semiinvoluta* Zone (at 38,2 Ma), whereas other two closely spaced horizons occur in the lower part of the *Globorotalia cerroazulensis* Zone (at 37,3 and 37,2 Ma) [2, 3]. It was also noted that microtektites and spherule horizons are depleted in $CaCO_3$, possibly as a consequence of carbonate solution caused by corrosive bottom water during periods of global cooling [2 , 4]. The age of the younger two microspherule horizons was subsequently revised, and was attributed to the latest *Porticulasphaera semiinvoluta* Zone [6]. Multiple Ir-anomalies, which suggest a sequence of closely spaced impacts during a period of 35,7-34,7 Ma (lower part of *G. cerroazulensis* Zone) were documented from deepmarine sediments in central Italy [7]. However, no spherules were found in association with those Ir-anomalies. Ref. [8, 11] differentiated true microtektites from glass spherules containing clinopyroxene. Spheroids with Ni-rich spinel were found in sediments of the lower part of the P16 Zone (35,7 Ma in age) at the Massignano section in Italy, in the horizon with Ir-anomaly [12].

Not only the number of impacts differs among various researchers, but also zonal boundaries (P 15 / P 16, P16 / P17) are attributed different ages by different authors [3, 6, 7, 12]. Thus, we will relay herein on biostratigraphical zonation, but also because we lack isotopic control of our sediment ages.

Late Eocene was a period of several well documented bolide impacts [13] (Table 1).

Table 1: Impact structures of Late Eocene age [13]

Impact structure	Location	diam. (km)	age (Ma)
Chesapeake Bay	U.S.A.	90	35.5 ± 0.3
Popigai	Russia	100	35.7 ± 0.2
Crawford	Australia	85	> 35
Flaxman	Australia	10	> 35
Mistastin	Canada	28	37 ± 1*
Wanapitei	Canada	75	37.2 ± 1.2

* age revised in 2006 [14]

At present time, only two Eocene impact structures are recognized of sources of tektites/microtektites or spherule layers. The American tektite strewn field is associated with Chesapeake Bay impact crater [15, 16], and microkrystites of Indian and Pacific ocean are associated with Popigai impact crater of Northern Siberia [17].

2. THE STUDIED AREA AND DEPOSITS

The studied area is located in Central Dalmatia, Croatian Adriatic, near the Solin city (Fig. 1). Geologically, the studied area belongs to the "External Dinarides" unit [18, 19] and it is made of two stratigraphically and paleogeographically distinct units: a) carbonate platform succession of the late Mesozoic to early Tertiray age, and b) Tertiary flysch and molasse clastics [20].

The eastern Adriatic flysch stratigraphically spans from Middle Eocene [21], Bartonian [22] to the late Miocene [23, 24]. In the studied area, it is of carbonate composition and is overlain by, as well as locally interfingers with conglomeratic Promina Beds which are interpreted as molasse (Fig. 2). The Dalmatian flysch can be subdivided into three informal flysch "zones"; the lower- , middle- and upper flysch zone [24, 25, 26]. These zones correspond to the syn-rift (lower- and middle flysch zone) and post-rift (upper flysch zone) successions of the basin fill [25, 26]. The Lower Flysch Zone (LFZ) is ca. 750 m thick, but poorly exposed. Here predominate megabeds, whereas other lithofacies and their groups, such as turbidites, heterolithic sediments and conglomerates are subordinate. The Middle Flysch Zone (MFZ) is represented by ca. 180-190 m thick olistostrome [27] which is a single-event deposit, and represents a boundary between the ponded basin (LFZ) and a wider one (UFZ) without significant ponding of gravity flows [26]. The Upper Flysch Zone (UFZ) is ca. 860 m thick, and comprises various types of turbidites (which occur in the lower part of the Zone only), heterolithic sediments, sandy marls, sandy calcarenites, and conglomerates. Conglomerate wedges occur in the upper part of the LFZ and throughout the UFZ. They are interpreted as alluvial fans and their distal wedges [25], and attributed to episodes of relative sea-level falls [28].

Detailed descriptions of all faces represented in the studied succession is beyond the scope of this paper, and we will focus only on spherule-bearing turbidites.

Turbidites encompass two types of beds: a) Bouma-type Ta-e and Tc-e turbidites, some of which attain up to 47 m in thickness, and b) megabeds which are defined by thickness > 10 m, and comprise two types of beds, based on the bed architecture: i) composite turbidites, and ii) complex beds [25, 26, 29, 30]. Megabeds are dominant bed-type in the LFZ, but in the UFZ occur restricted only to its lowermost part [26]. Composite turbidites are rare, only few being described in the literature. They are characterized by several lithologically uniform and normally graded thinning-upward units which are clearly erosive with contacts marked by slightly coarser debris, e.g. bed 2-7. In addition to current structures, the beds are also characterized by water-escape dish-and pillar structures, and convolutions of post-depositional origin. The 2-7 bed is made of 14 m thick calcarenite, and 24 m thick marls which comprise alternating massive and laminated units [29]. Complex beds are defined as bipartite beds composed of debrite in the lower part and turbidite above, with a clear transitional contact between the two [25, 26]. The thickest bed studied is 180-190 m

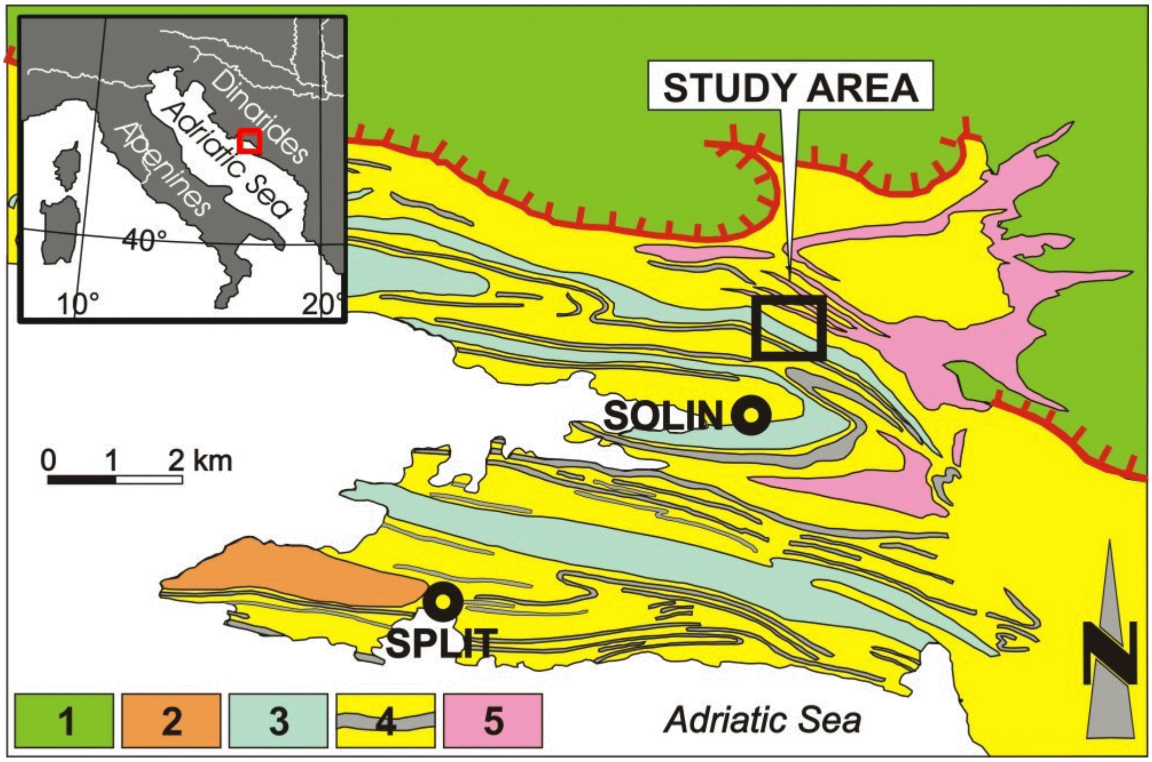

Fig 1: Simplified geological map of Central Dalmatia. Key: 1 = Mesozoic carbonates, 2 = Lower-Middle Eocene carbonates, 3 = K-S olistostrome, 4 = Middle-Upper Eocene flysch with megabeds, 5 = Eocene-Oligocene conglomerates. Map after [24], modified.

thick K-S olistostrome [25, 26, 27], which contains olistolites some of which reach up to 500.000 m^3 in volume.

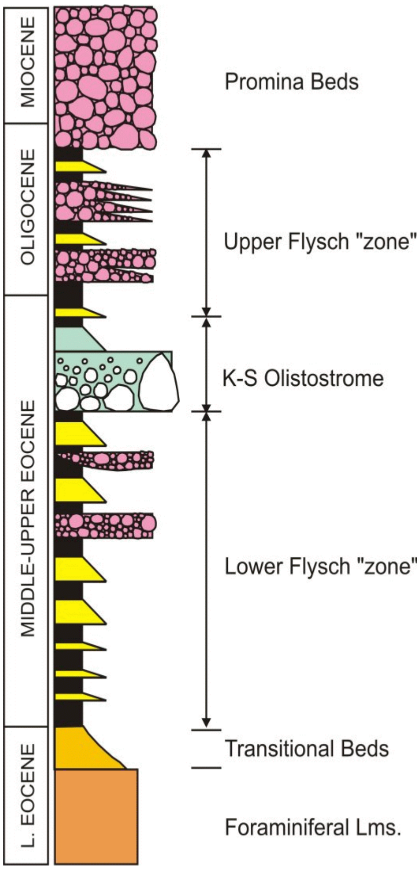

Fig.2. Depositional succession of Central Dalmatia.

Bouma-type turbidites were deposited from low-density turbidity currents [31]. The final stage in their deposition was from the ponded turbidity current tails to account for large thickness of turbidite marls.

Megabeds were deposited from turbidity currents with high initial volume, and lutites were deposited from ponded turbidity current tails. The composite turbidites were deposited from closely-spaced sequence of flows which could be treated as essentially a single depositional event. Sharp contacts of component units are probably a result of successive flow surges. Intervals of the massive marls were deposited from ponded turbidity current tail, but laminated intervals were probably deposited under influence of bottom waves, such as seiches, or bottom currents. The complex beds are also single-event deposits, deposited from large-volume gravity flows. Their lower part (debrite) was deposited by freezing of a debris flow, whereas their upper part was deposited from high-density turbidity current [31]. The initiation mechanism of such catastrophic events is commonly related to high-magnitude seismicity [32, 33, 34].

3. METHODS

The outcrop conditions allowed detailed sampling, and we attempted to avoid the weathering crust and altered sediments. Sampled were contacts of very finegrained arenite and marls in turbidites, turbidite marls at various levels above the bed base, and marl interbeds in heterolithic sediments. Typical sample was 100-200 grams, but the horizons with impactoclastic debris were successively re-sampled. To avoid contamination, samples were crushed in polyethylene bags, and disintegrated in 3 % solution of H_2O_2 and tap water, sieved through 65, 90, and 500 µ sieves and dried in microwave oven for 3-5 min. at 500 W. Mineral grains, spherules, microtektites and microfossils were hand-picked under stereo-microscope. Small magnetic spherules (ca. 60 µ across) were recovered by hand-magnet, although the procedure resulted in their magnetization. Chemical composition of spherules was made on JEOL JSM-6460LA electron microscope.

4. SPHERULE-BEARING BEDS

The studied turbidite succession comprises seven different stratigraphic horizons with glass spherules, metallic spherules, fragments of vesicular glass, and teardrop microtektites.

The spherules of *Globigerinatheka semiinvoluta* zone (former P 15, now E14 [35]) occur in the LFZ, ca. 20 m below the K-S olistostrome base. They occur in T_{a-e} turbidite bed 315. Although the K-S olistostrome was a candidate for an syn-impact bed, only rare scattered metallic spherules are found at various levels of its marl part.

The spherules of *Globigerinatheka index* zone (former *cerroazulensis* zone, P16, now E15) occur at six levels in the UFZ, which are stratigraphically referred to prominent sequence boundary in base of coarsegrained fan delta III [25] (SB) (Fig. 3). The first spherule horizon of this zone occurs in the bed 3-45 which is 3.5 m thick T_{c-e} turbidite 11,5 m below the SB. The second horizon is 5 cm thick marl layer of the 3-69 bed, located 50 cm below the SB. The third horizon is 2,5 m thick T_{b-e} turbidite 3-83 located 2,25 m above the SB. The fourth horizon is 1 m thick T_{c-e} turbidite 3-88 located 4,75 m above the SB. The fifth horizon is marl layer associated with heterolithic interval 2-5, located 85 m above the SB. The sixth horizon is 38 m thick composite turbidite 2-7 located 93,3 m above the SB. It yielded largest number of glass spherules, vesicular glass fragments, metallic spherules, and microtektites, which occur in largest number at arenite-marl transition, and exclusively in units of the laminated marl.

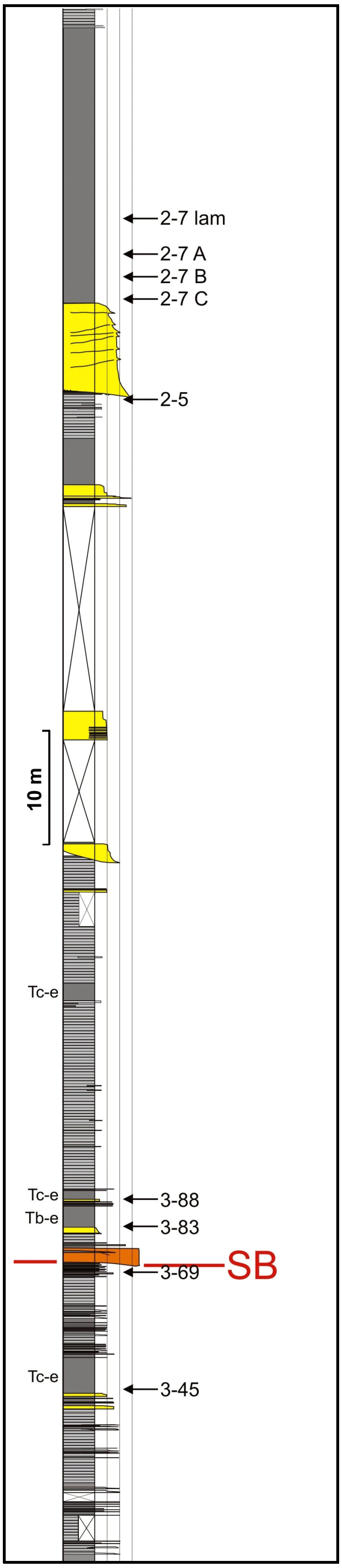

Fig. 4. Sedimentological log of studied sediments. *Globigerinatheka index* zone (E15).

5. IMPACT GRAINS

The spherules in *Globigerinatheka semiinvoluta* zone (E14) are up to 80 μ in diameter. The glass spherules are yellowish tinted and transparent, some are black opaque, whereas metallic ones are grey with metallic luster.

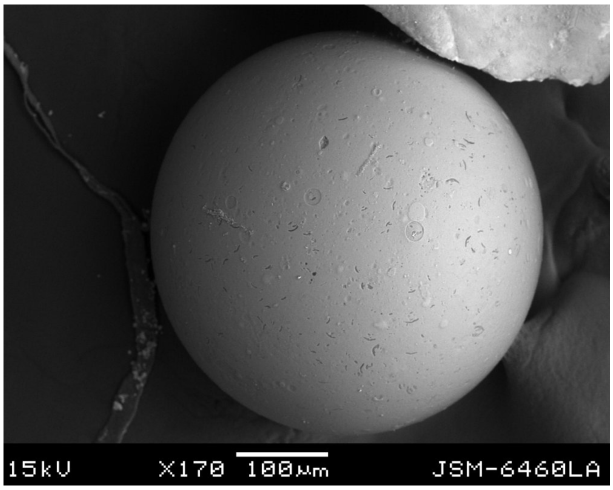

Fig. 4. Glass spherule 2-7C-6

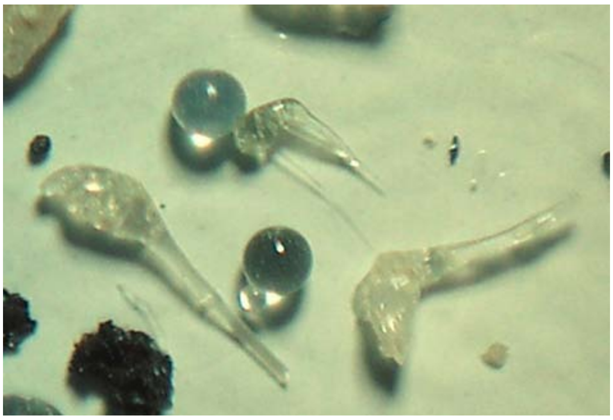

Fig. 5. Glass spherules and microtektites. Bed 2-7.

The glass spherules, vesicular glass, metallic spherules and microtektites in *Globigerinatheka index* zone (E15) are morphologically all very similar. The glass spherules are perfect spheres (Figs. 4, 5), 91 μ to 530 μ in diameter. Usually they are water-clear (Fig. 5), sometimes slightly dimmed, or with pearl luster. Sometimes small spherules are attached at the large ones, and close inspection (SEM) of their surface revealed small and shallow, flat-bottom, crater-like structures probably formed by escaping fluids. The metallic spherules are 80 μ to 180 μ in diameter. They are commonly highly magnetic, sometimes with metallic luster, sometimes dull. The fragments of vesicular glass measure 450 μ to 1000 μ across, and are made of whitish to yellowish, commonly untransparent glass. Teardrop microtektites are up to 1225 μ long, most commonly made of transparent milky glass. Sometimes they have one "tail", sometimes two (Fig. 5). The microtektite glass commonly comprises small vesicles with diameter up to 41 μ, and their surface is pitted with small fluid-escape craters.

Table 2: composition of typical spherule from the bed 2-7:	
SiO_2	28.90
Al_2O	--
Al_2O_3	--
Fe_2O_3	--
CaO	17.22
MgO	7.84
FeO	0.80
ZnO	0.50
TiO_2	0.42
MnO	0.36
CuO	0.19
Na_2O	0.28
K_2O	0.25
P_2O_5	0.23
SO_3	1.17
SO_2	--
CO_2	41.01
NiO_2	--
NiO	--
Cr_2O_3	--
L.O.I.	--
	99.17

6. DISCUSSION

Spherules of *G. semiinvoluta* and *G. index* zone differ in size and colour; the former are smaller, partly transparent, partly opaque, yellowish to brownish in colour, whereas the latter are larger and usually perfectly clear. The two very likely represent impactites of different impact events. We will try to address this hypothesis in continuation of our research.

Although spherules of the *G. index* occur at six (!) levels, they are all morphologically almost identical, they all have the same association of vesicular glass, metallic spherules, and mineral grains, so resedimentation can not be positively ruled-out as possible cause of stratigraphic repetition of one spherule horizon. However, many samples were analyzed from intermediate levels/beds, with no spherules or other impact grains found.

Composition of analyzed spherule from *G. index* zone (Table 2) shows significant difference from spherules of North American strewn field [36, 37, 38], as well as spherules from Italian sections attributed to Popigai impact [12]. The major difference is in low SiO_2 content (28,9 %), and higher CaO and MgO content. The difference is also marked by ZnO, CuO, P_2O_5, SO_3, and particularly by high CO_3 content, which are unreported in published data on Upper Eocene spherule composition.

7. CONCLUSION

The Central Dalmatian Upper Eocene flysch succession comprises two horizons of impact-derived spherules, the older in *G. semiinvoluta* and younger in *G. index* zone.

The composition of spherules recovered from the 2-7 composite turbidite indicates possible sedimentary target of a large impact, very likely composed of limestones and dolomites. Since their composition greatly differs from other Upper Eocene spherules, particularly North American strewn field, as well as Popigai-derived microkrystites, we speculate that the source of analyzed spherules is yet undiscovered Late Eocene large impact structure.

8. REFERENCES

1. Keller G., Eocene-Oligocene boundary reference sections in the Pacific. In: *Terminal Eocene Events* (eds. Pomerol Ch. & Premoli Silva I.). Dev. in Paleont. and Strat. 9, Elsevier, 209-212, 1986

2. Keller G., Late Eocene impact events and stepwise mass extinctions. In: *Terminal Eocene Events* (eds. Pomerol Ch. & Premoli-Silva I.). Developments in Paleontology and Stratigraphy 9, 403-412, Elsevier, 1986.

3. Keller G., Stepwise mass extinctions and impact events: Late Eocene to Early Oligocene. *Marine Micropaleontology*, vol. 10, 267-293, 1986.

4. Keller G., D'Hondt S.L., Orth C.J., Gilmore J.S., Oliver P.Q., Shoemaker E.M. and Molina E., Late Eocene impact microspherules: stratigraphy, age and geochemistry. *Meteoritics*, vol. 22, 25-60, 1987.

5. Hazel J.E., Chronostratigraphy of Upper Eocene Microspherules. *Palaios*, vol. 4, 318-329, 1989.

6. Miller K.G., Berggren W.A., Zhang J. and Palmer-Julson A.A., Biostratigraphy and Isotope Stratigraphy of Upper Eocene Microtektites at Site 612: How Many Impacts? *Palaios*, vol. 6, 17-38, 1991.

7. Montanari A., Asaro F., Michel H.V. and Kennett J.P., Iridium Anomalies of Late Eocene Age at Massignano (Italy), and ODP Site 689B (Maud Rise, Antarctic). *Palaios*, vol. 8, 420-437, 1993.

8. Glass B. P. and Burns C. A., Late Eocene crystal-bearing spherules: two layers or one? *Meteoritics*, vol. 22, 265-279, 1987

9. Glass B.P., Tektites and microtektites: key facts and inferences. In: *Cryptoexplosions and Catastrophies in the Geological Record, with Special Focus on the Vredefort*

Structure (eds. Nicolaysen L. O. & Reimold W. U.) Tectonophysics, vol. 171, 393-404, 1990.
10. Poag W.C. and Aubry M-P., Upper Eocene Impactites of the U.S. East Coast: Depositional Origins, Biostratigraphic Framework, and Correlation. *Palaios*, vol. 10, 16-43, 1995.
11. Glass B.P., Late Eocene Microtektites and Clinopiroxene-bearing spherules. In: *Terminal Eocene Events* (eds. Pomerol Ch. & Premoli-Silva I.). Developments in Paleontology and Stratigraphy, vol. 9, 395-401, Elsevier, 1986.
12. Pierrard O., Robin E., Rocchia R. and Montanari A., Extraterrestrial Ni-rich spinel in upper Eocene sediments from Massignano, Italy. Geology, vol. 26, 307-310, 1998.
13. Earth Impact Database, <http://www.unb.ca/passc/ImpactDatabase/Age.html> (Accessed: 26/6/2006)
14. Kelley S., Testing for clustering in the terrestrial impact record: progress through dating ancient craters. <http://www.rssd.esa.int/SYS/docs/ll_transfers/296311_kelley_pres.pdf> (Accessed: 28/6/2006)
15. Poag W., Powars D.S., Poppe L.J. and Mixon R.B., Meteoroid mayhem in Ole Virginy: Source of the North American tektite strewn field. *Geology*, vol. 22, 691-694, 1994.
16. Koeberl Ch., Poag W.C., Reimold U.W. and Brandt D., Impact Origin of the Chesapeake Bay Structure and the Source of the North American Tektites. *Science*, vol. 271, 1263-1266, 1996.
17. Whitehead J., Papanastassiou D.A., Spray J.G., Grieve R.A.F. and Wasserburg G.J., Late Eocene impact ejecta: geochemical and isotopic connections with the Popigai impact structure. *Earth and Planetary Science Letters*, vol. 181, 473-487, 2000.
18. Chorowicz J., Stratigraphie et tectonique d'un secteur de la Dalmatie moyenne, pres de Split (Yougoslavie). *Bull. Soc. géol. Fr. (7)*, vol. 11/6, 862-870, Paris, 1969.
19. Aubouin J., Blanchet R., Cadet J-P., Celet P., Charvet J., Chorowicz J., Cousin M. and Rampnoux J-P., Essai sur la géologie des Dinarides. *Bull. Soc. géol. Fr. (7). ser., 12*, 1060-1095, Paris, 1970.
120. Marjanac T. and Ćosović V., Tertiary Depositional History of Eastern Adriatic Realm. In: *Outline of the geology of the Dinarides and south Tisia with field guidebook* (eds. Pamić J. & Tomljenović B.), *Vijesti Hrvatskoga geol. društva* vol. 37, 93-103, 2000.
21. Piccoli G. and Proto Decima F., Ricerche biostratigrafiche sui depositi flyschoidi della regione Adriatica settentrionale e orientale. *Mem. Ist. Geol. Miner. Univ. Padova*, vol. 27, 1-23, 1969.
22. Benić J., Vapnenački nanoplankton i njegova primjena u biostratigrafiji krednih i paleogenskih naslaga Hrvatske. Doctoral Thesis. University of Zagreb. 1-159, 1983.
23. de Capoa, P., Radoičić, R. and D'Argenio, B., Late Miocene deformation of the External Dinarides (Montenegro and Dalmatia). New biostratigraphic evidence. *Mem. Sci. Geol.*, vol. 47, 157-172. Padova, 1995.
24. Kerner F., Gliederung der Spalatiner Flysch Formation. *Verhandl. Geol. Reichsanst*, vol. 5, 87-102, Wien, 1903.
25. Marjanac T., Evolution of Eocene-Miocene flysch basin of Central Dalmatia, Croatia. Doctoral Thesis, University of Zagreb, 1-348, 1993.
26. Marjanac T., Importance of megabeds for reconstruction of Paleogene flysch basin in Split hinterland (Middle Dalmatia). *Geol. vjesnik*, vol. 44, 201-213, Zagreb, 1991.
27. Marjanac T., Sedimentacija Kernerove "srednje fliške zone" (paleogen, okolica Splita). *Geol. vjesnik*, vol. 40, 177-194, Zagreb, 1987.
28. Marjanac T., Deposition of megabeds (megaturbidites) and sea-level change in a proximal part of Eocene-Miocene flysch of central Dalmatia (Croatia). *Geology*, vol. 24, 543-546, 1996.
29. Marjanac T., Anatomy of a composite turbidite in flysch of middle Dalmatia (Yugoslavia). Abstracts 8. I.A.S. Reg. Mtg., Tunis. 338-339, 1987.
30. Marjanac T., Reflected sediment gravity flows and their deposits in flysch of Middle Dalmatia, Yugoslavia. *Sedimentology*, vol. 37, 921-929, Oxford, 1990.
31. Lowe D.R., Sediment gravity flows: II depositional models with special reference to the deposits of high-density turbidity currents. *Jour. Sed. Petrol.*, vol. 52, 279-297, Tulsa, 1982.
32. Johns D.R., Mutti E., Rosell J. and Séguret M., Origin of a thick, redeposited carbonate bed in Eocene turbidites of the Hecho Group, South-central Pyrenees, Spain. *Geology*, vol. 9, 161-164, 1981.
33. Labaume P., Mutti E. and Séguret M., Megaturbidites: A Depositional Model From the Eocene of the SW-Pyrenean Foreland Basin, Spain. In: *Megaturbidites* (eds. Doyle L.J. & Bourrouilh R.). Geo-Marine Letters, vol- 7, 91-101, New York, 1987.
34. Séguret M., Labaume P. and Madariaga R., Eocene seismicity in the Pyrenees from megaturbidites of the South Pyrenean Basin (Spain). *Marine Geology*, vol. 55, 117-131, Amsterdam, 1984.
35. Berggren W.A. and Pearson P.N., A revised tropical to subtropical paleogene planktonic foraminifera zonation. *J. Foram. Research*, vol. 35, 279-298, 2005.
36. D'Hondt S.L., Keller G. and Stallard R.F., Major element compositional variation within and between different Late Eocene microtektite strewnfields. *Meteoritics*, vol. 22, 61- 79,1987.
37. Glass B.P., North American tektite debris and impact ejecta from DSDP SIte 612. *Meteoritics*, vol. 24, 209-218, 1989.
38. Dressler B.O. and Reimold U., Terrestrial impact melt rocks and glasses. *Earth-Science Reviews*, vol. 56, 205-284, 2001.