CHEMICAL COMPOSITION OF MIDDLE PERMIAN GLASS SPHERULES IN EXTERNAL DINARIC ALPS, CROATIA M. Čalogović[1], S. Fazinić[1], T. Marjanac[2], J. Sremac[2], Lj. Marjanac[3] and A. Šimičević[4], [1]Ruđer Bošković Institute, 10000 Zagreb, Croatia (Marina.Calogovic@irb.hr, Stjepko.Fazinic@irb.hr), [2]University of Zagreb, Faculty of Science, Department of Geology, 10000 Zagreb, Croatia (marjanac@geol.pmf.hr, jsremac@geol.pmf.hr), [3]Institute of Quaternary paleontology and geology CASA, 10000 Zagreb, Croatia (ljerka@hazu.hr), [4]Franka Lisice 4, 23000 Zadar, Croatia (anasimicevic@yahoo.com).

Introduction: The section of Middle Permian deposits on the Velebit Mt., Croatia, is located 100 km from the nearest industrial city in a mountain roadcut which exposes thick succession of shales interbedded with shallow-marine dolomitized limestones of reefal and peri-reefal origin (Fig. 1) [1]. Glass spherules [2] were found in sediments of the *Neoschwagerina craticulifera* biozone (Late Roadian/Early Wordian) during recent study of intra-Guadalupian ecological crisis and recovery. After the initial discovery, additional sampling and sub-sampling was done along the whole length of the outcrop to check for possible contamination and to find horizon with most spherules. Spherules were found only at 2 of 10 sampling locations; in "basal" black shales 5.5 m below the first reefal limestone in the succession, and in a shale bed 1.5 m below the second reefal limestone (Fig. 2 in [2]).

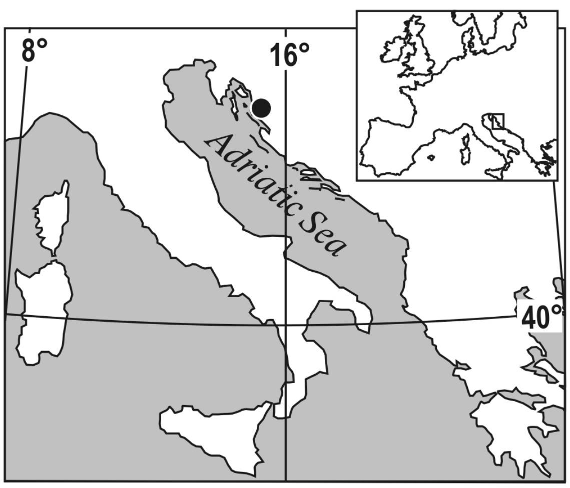

Fig. 1. Position of studied shales (dot) in Dinaric Alps.

Morphology and types of spherules: The spherules are glass-transparent, essentially colorless, but few are tinted yellowish to brownish (Fig. 2). The majority of spherules are perfect spheres 180 – 620 µm in diameter, whereas ellipsoidal glass grains are fewer, but up to 1090 µm long. Teardrop-shaped glassy grains are rarest and up to 600 µm long.

Some spherules are made of massive glass, but some contain small vesicles, sometimes aligned in "laminae". Some broken spherules reveal their homogenous structure, whereas some are hollow in their centers - resembling a glass balloon.

Some transparent spherules are partly coated with thin white amorphous crust as a kind of "cement" (Fig. 2). The same material also occurs as larger chunks, pitted with holes which probably nested glass spherules, herein referred to as "matrix". The brownish spherules and droplets are much fewer and are not covered with the "cement" crust.

A number of transparent spherules are fused together making clusters, usually composed of a larger spherule with several smaller ones attached.

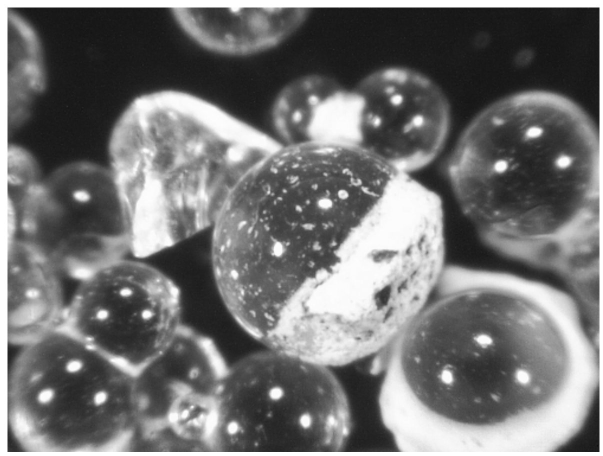

Fig. 2. The transparent spherule in the centre is 250 µm in diameter and half-covered with white carbonate "cement" crust. Two fused spherules are in the lower left corner.

Research methods: Spherules and their "cement" were analyzed at the Rudjer Bošković Institute Accelerator facility using PIXE Spectroscopy in high vacuum at the ion micro-beam end-station. The 2 MeV proton beam of about 50 pA current was focused to several µm in size and positioned on selected areas on samples. X-rays from the selected areas of the samples were collected by PGT Si(Li) detector with 8.4 µm thin Be window and Al "funny filter" (75 µm thick with 2.4 % hole area). Quantitative analysis of collected PIXE spectra was performed using fundamental parameter approach with GupixWIN Software [3]. Iterated matrix solution algorithm was used assuming that all the elements are present as oxides with the option of normalization to 100%, except in the case of metallic droplet where it was assumed that invisible elements were not present. Glass standard NIST 620 was used for calibration.

Chemical composition of spherules: Two types of spherules were analyzed; a) transparent spherules and ellipsoidal glass grains, and b) brownish-tinted spherules. These were complemented by analysis of the "cement" crust, "matrix", and the teardrop grain.

Composition of analysed spherules and glass grains in wt %				
	transparent	brownish	"cement"	"matrix"
Na_2O	15.1-21.27	10.68	0.00-1.13	0.73*
MgO	2.69-3.43	2.02	0.00-0.65*	0.51*-1.58
Al_2O_3	1.13*-5.40	2.83	7.44-13.72	3.63-14.62
SiO_2	71.46-83.65	69.74	4.17-6.20	1.09*-11.94
SO_2	0.13*-1.88	-	0.00-0.32*	0.26*
Cl	0.00-0.043	0.14*	0.00-0.14*	-
K_2O	0.13*-0.82	-	0.58*-0.92*	0.65*
CaO	10.91-14.55	20.71	5.60-72.20	62.82-74.15
TiO_2	0.03*-0.16*	0.14*	18.35-78.59	15.63-21.69
MnO	0.007*-0.1*	0.35*	-	0.099*
Fe_2O_3	0.11*-0.37	-	0.84-2.83	0.86

* measured at the detection limit

Discussion: The table shows quite consistent chemical composition of transparent spherules and ellipsoidal grains, regardless of their size and shape, which differs from the composition of brownish spherules, "cement" and "matrix".

The chemical composition shows that majority of transparent glass spherules are made almost entirely of Si and Ca oxides, whereas brownish spherules are enriched in Ca (63%), but depleted in Na (-41%) and Mg (-34%) oxides. The "cement" crust and "matrix" have similar compositions. The "crust" has very wide range in the amount of CaO, but the highest value is similar to that of the "matrix". The "crust" and "matrix" are enriched in Ti oxides, but "cement" has significantly higher maximal concentration (78.59 %). Both "crust" and "matrix" are low in Si and Na oxides. The teardrop grain is essentially made of Fe (84 %) with small addition of Ti (3%).

The chemical composition of spherules from the "basal" shale and from the higher horizon below the second reefal body [2] is within the measured range, with very small variation. The compositional uniformity of glass spherules at the studied section documents their identical origin and reworking from the "basal" shales.

The stratigraphic position of spherules within the Guadalupian *Neoschwagerina craticulifera* zone, possibly Roadian/Wordian boundary, which is characterized by ecological crisis at the studied section, opens a question of their origin.

Chemical composition of the majority of spherules indicates rather high content of Si and Ca and very low content of Ti oxides (at the detection level), which significantly differs from the composition of "cement" and "matrix" which are rich in Ca and Ti oxides and depleted in Si, and the droplet which is essentially made of Fe. Consequently, the origin of spherules and other glass grains found at the Velebit Mt. Middle Permian section is unrelated to the Emeishan flood basalts, which differ chemically and in age [4]. The presence of shocked quartz grains [2] and chemical diversity of spherules and glass grains in the studied section may be explained by an asteroidal impact into a mixed sedimentary target, possibly offshore to account for the formation of tsunami deposit.

Conclusion: The difference in composition of glass grains, spherules and "matrix" indicates their condensation from melts of different chemical compositions which were immiscible in reduced gravity, and originated from melting of different source-rocks. The "matrix" is Ca-rich and Si-poor, whereas the transparent spherules are Si-rich and Ca-poor, so both inevitably originated from different source-rocks which might have been carbonates and siliciclastics, respectively. However, the Fe-rich melt which formed the teardrop grain (micro-tektite) may bear geochemical signature of a space body during its passage through the atmosphere, but for its characterization more research is still due.

Reworking of spherules from the "basal" shales must have occurred during subaerial erosion of the exposed spherule-rich shales during relative sea-level falls and resedimentation of the debris in shallow anoxic lagoons.

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