FIRST DISCOVERY OF MIDDLE PERMIAN GLASS SPHERULES IN EXTERNAL DINARIC ALPS, CROATIA - EVIDENCE OF AN OCEANIC IMPACT?

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Introduction: Biotic crisis at the Guadalupian/Lopingian boundary is well known in Neotethyan realm, but Permian section of the Central Velebit Mt. (External Dinaric Alps) in Croatia (Fig. 1) bears evidence of an earlier, intra-Guadalupian event which is biostratigraphically located in *Neoschwagerina craticulifera* biozone (Late Roadian/Early Wordian).

The studied section comprises thick black shales interbedded with reefal limestones and calcareous clastics composed of peri-reefal skeletal debris. The reefal bodies are interpreted as morphological and ecological cement reefs draped with peri-reefal clastics [1] and bounded by erosional bases and tops.

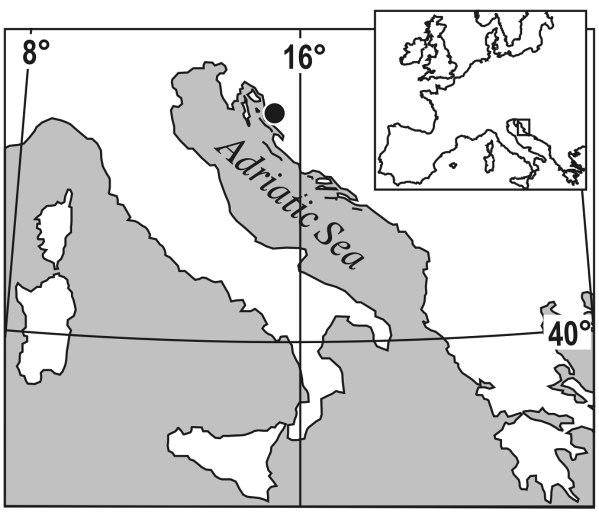

Fig. 1. Position of the studied Guadalupian sediments in Dinaric Alps.

Spherule-bearing horizons: Glass spherules were found at two horizons; in black shales 5.5 m below the first reefal limestone unit (A), and in a shale bed 1.5 m below the second limestone unit (B, Fig. 2). The first spherule horizon is 0.3 m thick "basal" cross-bedded shale; thin-bedded in the lower part and foliated in the upper, that underlies deformed shales which were interpreted as a submarine slump or possible large water-expulsion structure.

Spherules occur in first 25 cm, and disappear in the uppermost 5 cm of the bed. No spherules were found in shales within the possible dewatering structure, nor in several other sampled horizons.

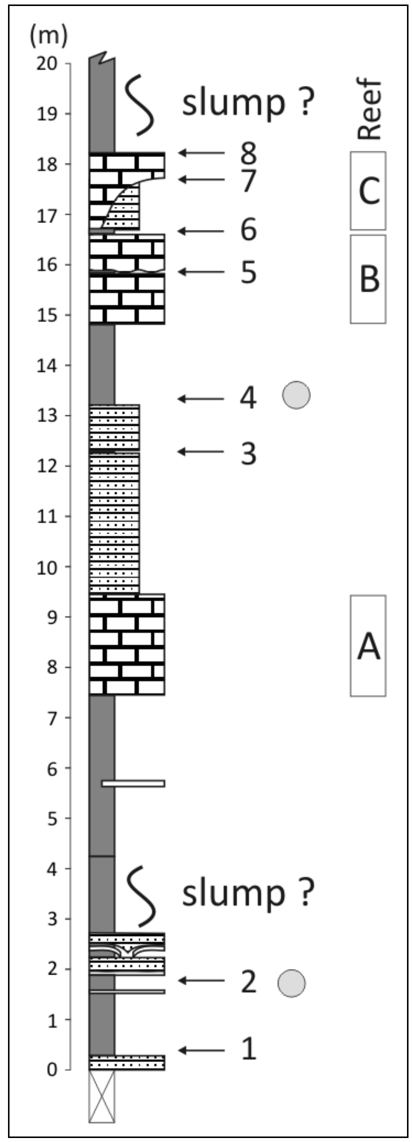

Fig. 2. Log of reefal limestones succession and sampling locations 1-8. Spherules are found only in loc. 2 and 4.

The "basal" shales are marked by pronounced change in spongal communities; calcisponges predominating below and silicisponges above, and comprise marine micro- and macrofauna (dominantly foraminifers, dasyclad algae and sponges). This shales also comprise well rounded lithoclasts (oolitic limestones, afossiliferous limestones, dolomites) 0.25 to 10 mm in diameter, and mineral debris (quartz, plagioclase and feldspars). Some quartz grains are shocked, with two sets of PDF's at sharp angles.

The shales are fissile, compacted, whereas one horizon in approximately middle position within the unit is extremely vesicular. The voids are open and were presumably formed by the escaping gas (? methane). No other shale horizon on the studied outcrop shows the same structure, neither the compositional diversity of the spherule-rich shale unit.

Morphology of spherules: Spherules (Fig. 3) are commonly clear glass spheres 180-620 µm in diameter. Several glass spherules may be fused together making relatively large clusters of smaller spheres (30-60 µm in diameter) surrounding a bigger one. In addition to spheres, there also occur large irregular ellipsoidal glass grains which attain more than 1000 µm in length, and 600 µm long teardrop brown glassy grains. Most spherules are water-transparent, but few are yellowish to brownish-colored.

Spherules are commonly massive, but some are hollow in the middle, and some comprise tiny vesicles which are sometimes arranged in "laminae". The surface of vesicle-rich spherules is pitted with shallow degassing craters.

Some spherules are partly covered by thin white amorphous "cement" crust (Fig. 2 in [3]). Morphologically identical are grains of homogenous white dull glass which host spherule casts.

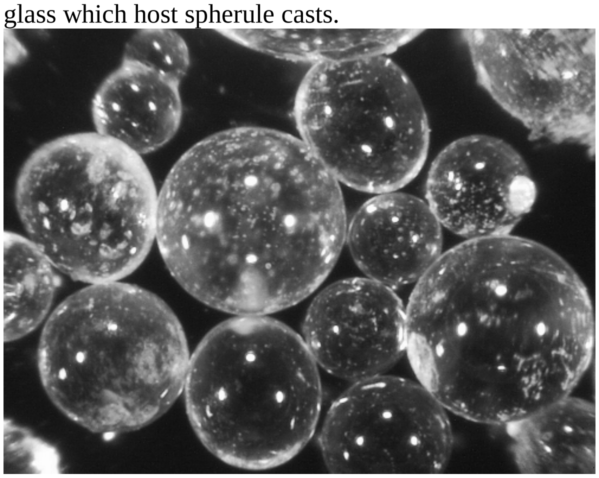

Fig. 3. Transparent spherules, large ones are 300 µm in diameter.

Composition of spherules: The transparent glass spherules are composed primarily of Si and subordinate Ca and Na oxides with minor compositional variations. The yellowish-tinted spherules are slightly richer in Ca, but the content of Na and Mg oxides is lower by 41-34% respectively, whereas the teardrop grain is made almost entirely of Fe. The white "cement" crust is made of Ca with high percentage of Ti, but depleted in Si oxides. The "matrix" is also largely made of Ca, enriched in Ti (but less than "cement" crust) and low in Si oxides [2].

Spherules from different horizons within the "basal" shale unit (sub-sampling was ca. 4 cm apart) have identical Si-rich chemical compositions, morphology and association with Ti-rich crusts, which all point to the same source/event.

Discussion and conclusion: The spherule-rich shale unit is interpreted as possible tsunami mass-flow deposit because of its structure, mixing of debris from terrigenous sources (outsized lithoclasts) and shallow marine source (foraminifera, dasyclad algae, sponges, gymnocodiaceans) which was below the depth preferred by the reef builders (sponges and encrusters) [3]. The vesicular shale horizon may have been formed by the escaping gas formed by decay of trapped organic (? plant) matter. Consequently, the spherule-rich shale is interpreted in terms of single-event bed which was formed semi-contemporaneously with the spherule-producing event.

The teardrop grain rich in Fe was formed as a melt was falling through the atmosphere, whereas perfect spherical and spheroidal Si and Ca-rich spherules were formed by rapid condensation and cooling of the melt which trapped escaping volatiles (Oxygen?) in tiny bubbles in the spherule interior, only few escaping at the surface. The compositional differences of spherules and amorphous Ca and Ti-rich glass indicates their origin from different melts created by the same event, very likely an impact into carbonate and siliciclastic target rocks, the interpretation also supported by presence of shocked quartz grains. The target must have been oceanic to account for generation of a tsunami which reworked debris from marine and terrigenous sources and dispersed spherules throughout the thickness of the resultant shale bed.

The occurrence of spherules at two horizons, below the reef bodies "A" and "B", and in small number at several other sampling locations is very likely a consequence of reworking, because reefal bodies are underlain by erosional surfaces probably caused by regional sea-level falls.

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Acknowledgment: This research was partly funded by research projects 119-0000000-1164 (T.M., Lj.M.), 119-1951293-1162 (J.S.), 0098013 (S.F.) of the Ministry of Science, Education and Sport of the Republic of Croatia.