Carpth. J. of Earth and Environmental Sciences, Vol. I, No. 2, p. 73 – 80

NEW RESULTS ON MAGNETIC SPHERULES FROM HUNGARY

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Abstract: Magnetic spherules were systematically collected and investigated from Pleistocene terrestrial sediment in Southern Hungary. By the chemical analysis: Fe, Fe(Mn), Fe(Ni) and glassy (silicate) spherules can be distinguished. Some of them have characteristic feature suggested extraterrestrial origin: Ni-bearing crust, Ni-rich core and especially platinum group nuggets with unique chemical composition. Their formation can be a meteorite ablation process.

Key words: spherules, extraterrestrial origin, Pleistocene sediment, Ni-rich core, platinum group nuggets

1. INTRODUCTION

It was more than a century ago when the first spherules of presumed cosmic origin were discovered in snow samples by Nordenskjöld, Swedish geologist and explorer (Nordenskjöld 1874) and in deep-sea sediments during the Challenger Expedition (1874-1876) (Murray 1876). In the last century there were new impulses for investigations: so the revelation of the iridium and osmium anomalies in deep-sea sediment as a good indicator for cosmic accretion matter (Barker and Anders 1968) and later a hotly disputed report about extraterrestrial cause for the Cretaceous-Tertiary extinction (Alvarez et al. 1980). Extraterrestrial spherules have been found in different places so as in deep-sea sediments, ice layers (Blanchard et al. 1980, Yamakoshi 1994), sedimentary rocks (Bi et al. 1993) or around the meteorite craters (Raukas and Tiirmaa 2000). Spherules of volcanic and anthropogenic origin also are frequent. The spherule researches can be use to different aims. So the stratigraphical and chronological determined distribution of particles can give good means to look for correlations with local, regional and global events or the spherules studies can help in reconstruction of meteorite craters. Nowadays the formation of spherules discovered on the surface of Mars (Opportunity, 2004) is an interesting question. Spherule researches have near ten years history in Hungary (Detre et al. 2002). In recent work the spherules from Pleistocene sediment (South Hungary) were studied by stratigraphical position. Here we are reporting about some of spherules having particular property with its metal core or nuggets suggested their cosmic origin.

2. GEOLOGICAL SETTING AND METHODS

About 50 m thick Pleistocene sediment was systematically sampled making use of three dug well and a borehole. The sediment covering a Palaeozoic granite formation consists of stratigraphical well-determined different loess and paleosoil sequences (Marsi 2002). 182 samples (2-3 kg/sample) were collected by 40 cm from wells while from borehole with some larger distances. After treatment with hydrogen peroxide and fractionation by grain size the magnetic spherules were concentrated using magnetic collection in two fractions (1.00-0.06mm and <0.06mm). The selection and first investigation of spherules were made under optical microscope. In the fraction of smaller grain size spherules were found in 41 samples, while in the other fraction 59 samples out of collected 182 ones contained magnetic spherules. This latter fraction was investigated more detailed. The sphere pieces were picked out manually under a binocular microscope. Approximately 200 spherules were recovered. Counting the spherules originated from different deepness the stratigraphical-frequency diagram can construct giving new data to look for correlations (see Fig. 1.). The morphological and chemical analysis of selected spherules were made by an AMRAY 1830I/T6 scanning electron microscope equipped with MORAN energy dispersive X-ray spectrometer using 20 keV acceleration potential, 1-2 nA beam current and standardless analysis file of the instrument.

3. RESULTS

The diameter of investigated spherules is between 40μm and 500μm. Generally their sizes are between 0-200μm (99±28μm), only some of them occur in the region of 200-500μm.

The colour, surface texture and morphologies of the spherules show some differences. There are shiny and dull pieces mainly with metallic, black or sometimes dark brown colour. Most of them are regular or nearly perfect sphere in shape. Rarely can be found drop-like spheroid forms as well suggesting these particles are originated from a molten material with rapid cooling. These shapes are assumed to form in the lower atmosphere from the molten surface of meteorite and have no time to develop rounded forms like the perfect spheres formed in the upper atmosphere (Yamakoshi 1994). In the case of glassy spherules the gas escaping bubbles and the Fe-bearing crystal forms also refer to the molten source.

By chemical composition four different types of measured particles can be distinguished: Fe, Fe(Mn), Fe(Ni) and glassy (silicate-bearing) spherules (Fig. 2.). The analyses were made on the surface of the particles; the investigations of polished sections are planed.

The first three types have smooth or rough surface depending on the size and shape of the covering crystals. Dendroid like cooling structure, well developed crystals

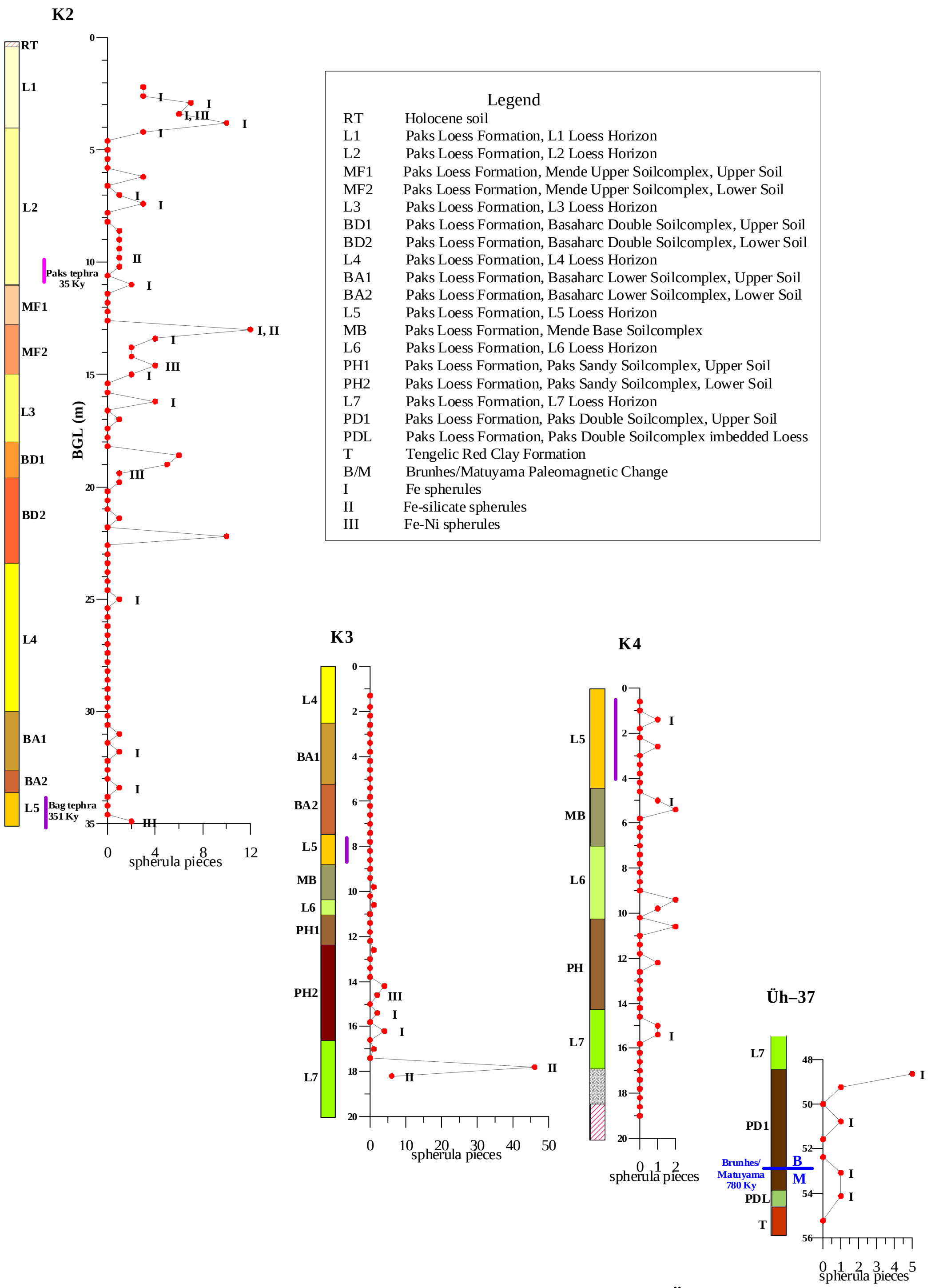

Fig. 1. Stratigraphical column of K2, K3 and K4 dug well and Üh-37 borehole with the spherule diagrams and tephra horizons

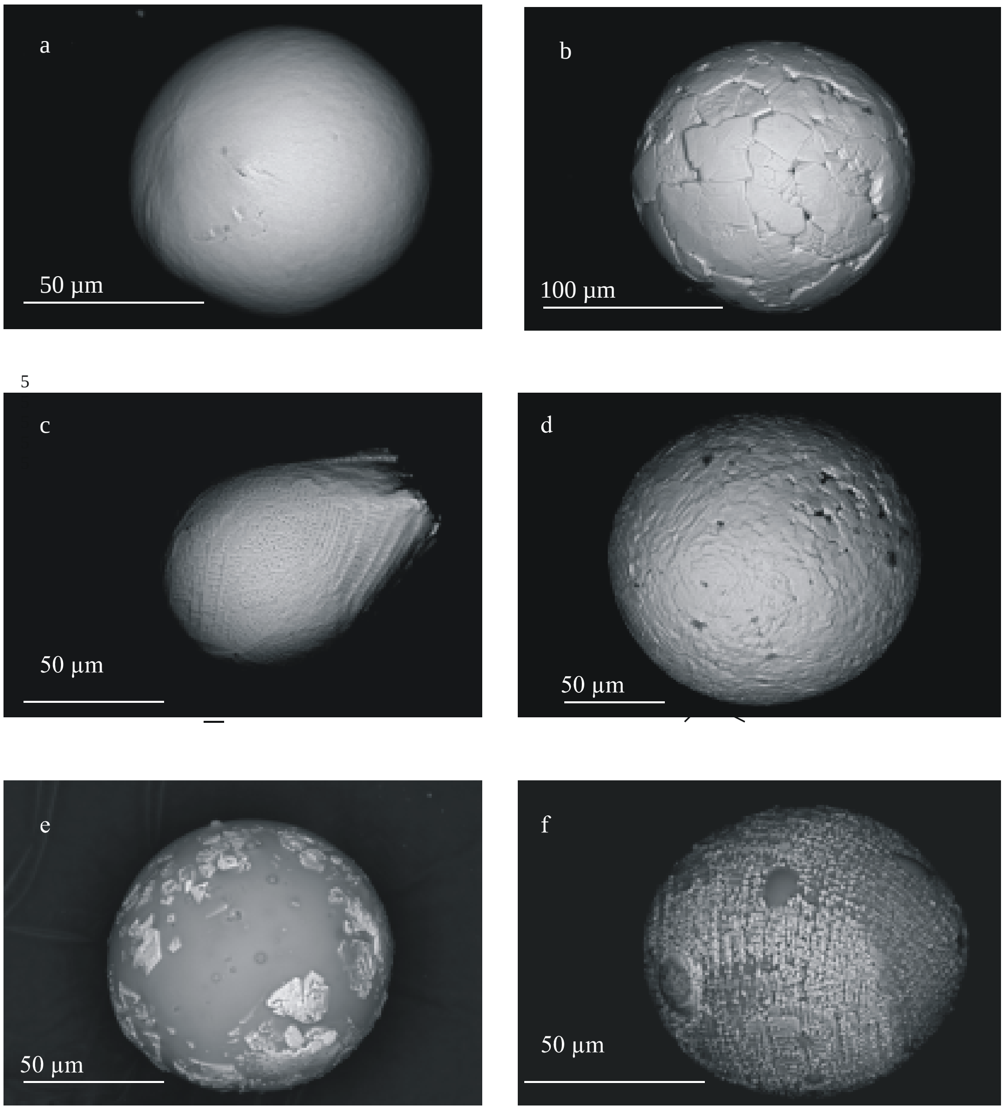

Fig. 2. BEI of different types of spherules: Fe spherule with fine crystal stucture (a), Fe(Mn) spherule with large crystals (b), drop-like Fe spherule (c), Fe(Ni) spherule with smooth surface (d),glassy spherules decorated with bubbles, more or less covered by Fe-oxide crystals (e,f)

with different size and fitting or peeling structure can be observed, while especially Ni-bearing pieces show slightly rounded form and corrosion-like pattern. The Mn-content is generally between 0.3-1.0wt%, while the Ni-content varies between 0.9-6.3 wt% on the surface of above mentioned type of spherules. The glassy spherules can be characterized by surface more or less covered with Fe-bearing crystals (magnetite), sometimes they present bubbles due to gas evolution and rapid cooling.

In some cases the cosmic origin can be assumed after SEM+EDX investigations.

Ni-content may refer to cosmic origin of spherule. We have identified this type in six cases

(Fe(Ni)-spherule group, Fig. 2.).

— In one of the particle of Fe(Ni)-spherule group a Ni-Fe-Co core (Ni: 33.0 wt%, Fe: 22.0 wt% and Co: 1.0 wt%) can be observed owing to damage of the covering pure iron oxide crust (Fig. 3.). Similar spherules of extraterrestrial origin have been discovered in many places e.g. deep-sea sediments (Blanchard et al. 1980) and terrestrial sediments as well (Bi et al.1993). It is noteworthy to mention that the later publication reported about a large number of Ni-Fe alloy spherules recovered also from Pleistocene terrestrial sediments (as in our case), in Alberta, Canada. These Ni-bearing spherules represent the ejected Fe-Ni core of cosmic spherules.

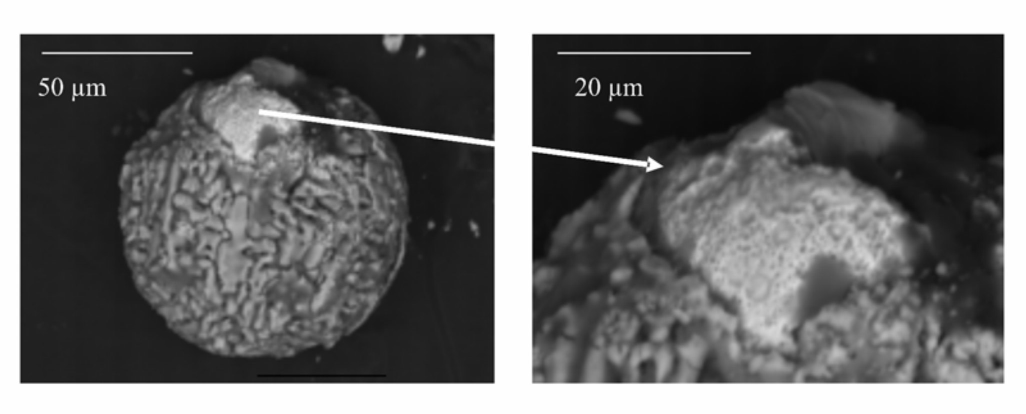

Fig. 3. BEI of spherule with Ni-rich core (white part) covered by pure Fe-oxide (gray)

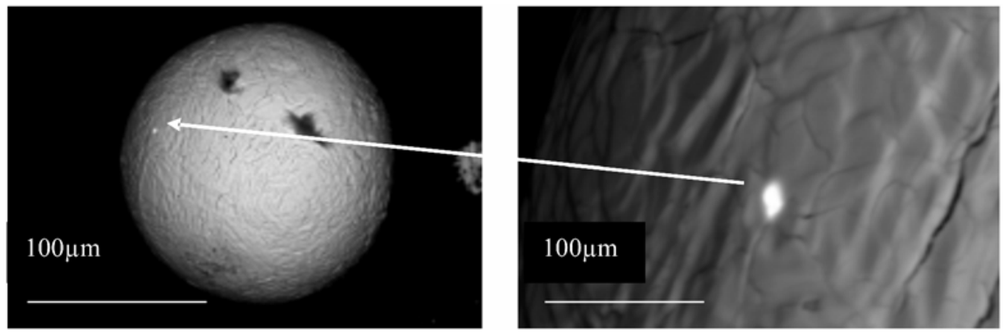

Fig. 4. BEI of Fe(Ni) spherule with nugget rich in platinum group elements (PGN). The nugget is near the surface and can observe as a bright spot between the covering crystals

— Two of the Ni-bearing spherules have a separated phase containing platinum group elements. One of them can be seen only as a little (approx.1x2 µm) bright spot between the covering crystals (Fig. 4). The other one appears on the top of the spherule as a small (near 3µm) sphere just escaping from the surface (Fig. 5.). These types of platinum group nuggets (PGN) were first discovered in deep-sea sediments (Brownlee et al. 1984) and later a tiny nugget has been reported from a condritic spherule (Misava et al. 1989). The measured chemical composition of the crust layer of the two PGN-bearing spherules (Fig 4. and 5.): Fe (93.9 and 99.1wt %) and Ni (6.1 and 0.9wt %) respectively. The composition of two PGNs can be seen in Table 1. with the data of the PGNs from deep-sea sediment (Brownlee et al. 1984).

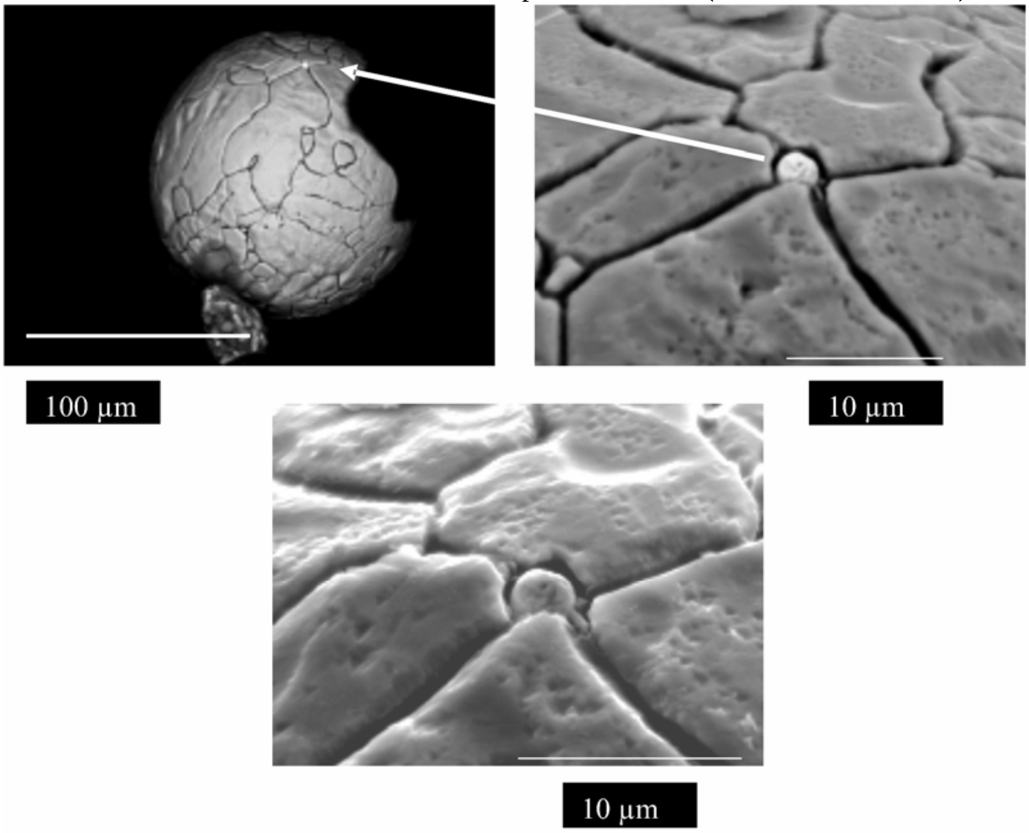

Fig. 5. BEI of Fe(Ni) spherule with PNG. The bright small sphere can be observed as it escaping from the surface showing strange cracks (upper two pictures) and a SEI from the PGN with slightly corroded surface around it (lower picture)

The unique composition and ratio of elements (compared to the solar abundance; Os=1.0) in our PGNs are similar to the data of PGNs from deep-sea sediment and confirm the extraterrestrial origin.

Similar metal nuggets are not easy to find even in the polished section because of the small size and varying positions of the nuggets inside of the spherules. Brownlee and co-workers only four PGNs could observe in polished sections of 110 spherules, while near in each of the sequentially (by 1-2 µm depth intervals) polished samples could find them.

The glassy spherules are more or less covered Fe-oxide crystals (Fig. 3.); in the glassy parts Si, Mg, Al, K, Ca, Ti and Fe can be detected in variable rations; they have probably volcanic origin.

4. CONCLUSION

The formation of extraterrestrial spherules with Ni-rich core or with PGNs (Brownlee et al. 1984) can be imagined as a meteorite ablation process. A meteorite is heated and metal droplets will be ablated from the surface during its entry and traversing in atmosphere, where owing to high-temperature oxidation a growing iron oxide shell develops leaving the elements more noble than iron (Ni, Co and the platinum group elements) inside in the molten metal core. During the progress of oxidation the metal core is getting continually richer in nickel. The following oxidation process can finally lead to the formation of PGN. During trajectory in atmosphere the Ni-rich core or PGN can move to the surface of spherule or can be ejected (Fig. 3) because of density differences between core or PGN and the host molten oxide.

The form, chemical composition and structure of the cosmic spherules depend on a lot of facts, among them the composition of meteorite type ablated, entry angle, velocity and so the temperature of oxidation resulting many variation of spherules. Our investigations finding extreme rarely discovered spherule types can confirm the assuming ablation process of meteorites.

The abundances of platinum group elements (PGE, refractory siderophile elements) may be different by meteorites. It is worthy of notice that the enrichment of PGEs was observed in isolated part of Ca-Al-rich inclusions (CAIs) as very small (um-sized or smaller) refractory metal nuggets and as metal-rich opaque assemblages (summarized in: Planetary materials, ed. by Papike 1998). In lot of cases these isolated parts of CAI have condrite-normalised PGE patterns (Campbell et al. 2001). The Ca-Al-rich inclusions condensed in early solar nebula and occur mainly in carbonaceous chondrites, so we can account them as one of the sources for such type of spherules.

In the case of extraterrestrial spherules a correlation can be found on the ground of stratigraphical-frequency diagram (Fig. 1.). Two of our Fe(Ni) spherules - as to stratigraphical position and age (L1 Loess Horizon, 20 000 years) - may correlate the Canadian Fe-Ni spherule horizon (Bi et al.1993).

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Received at 17.11.2006
Accepted for publication 11. 12. 2006