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Micro-scale magnetic grains from shallow water sediments of the Gulf of Gdańsk

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Abstract

Three cores recovered from the Gulf of Gdańsk in 2006 contain magnetic spherules of different origins. According to their chemical compositions and morphological features the magnetic grains were divided into two groups: (1) anthropogenic spherules primarily composed of SiO_2, Al_2O_3 and Fe_2O_3; (2) Fe-oxide spherules of extraterrestrial origin. These two groups are present in the surface sediments, indicating they are products of both man-made pollution and an influx of extraterrestrial matter. The presence of anthropogenic dust in the marine sediments is a record of pollution from nearby industrialized areas. On the basis of the presence of these spherules a tool could be developed for studying sedimentation rates in the marine sediments. However more precise studies are required to develop this method.

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INTRODUCTION

The activity of man increasingly influences the natural environment; the marks of such activity being visible in the geological record.

The primary aim of this study was to determine the presence of magnetic spherules of extraterrestrial origin in sediments of the Gulf of Gdańsk (Fig. 1). Such objects have been found not only in the vicinity of meteoritic impacts craters (Marini et al. 2004, Stankowski et al. 2006, Uścinowicz 2008a,b), but also in deep ocean sediments of relatively slow deposition (Crozier 1960; Brownlee et al. 1983; Taylor, Brownlee 1991; Toppani et al. 2001). As a result of these reports the presence of cosmic spherules was investigated in marine deposits of epicontinental sea.

However to moderate surprise the majority of recovered spherical particles appeared to be of anthropogenic origin. This induced the author to analyze the problem and to revalue the aims of the studies. That is why the aim of this paper is to characterize the origins of magnetic, micro-scale grains from the Gulf of Gdańsk independently to their origin. The presence of these deposits (products of burning solid fuels) might be further used to examine sedimentation of relatively shallow water marine deposits.

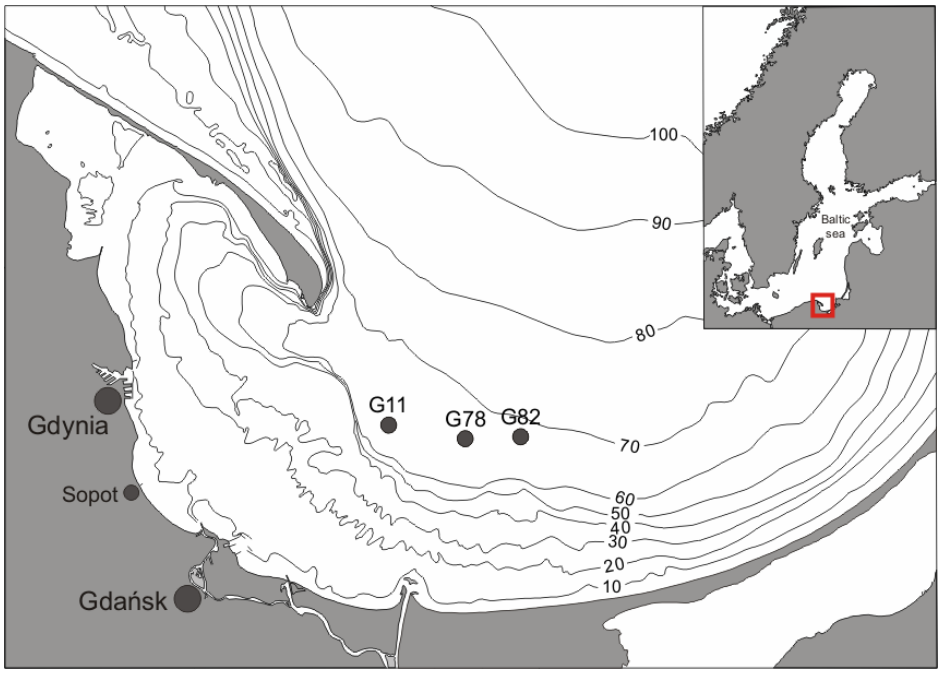


Fig. 1. Location of the study area with sites of core recovery marked.

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Characterization of the study area (sedimentary processes and sediments in the Gulf of Gdańsk)

The Gulf of Gdańsk is located in the southern part of the Baltic Sea. It largely lies close to Polish coast, with the eastern margin fringing the Russian coast. The Gulf of Gdańsk acts as a sedimentation basin of an epicontinental sea. Geologically, it includes the southern part of the Gdańsk Basin. The distribution of sediments on the seabed of the Gulf of Gdańsk is primarily dependent on the local hydrodynamic conditions, caused by the coast and seabed topography, as well as from the palaeogeography of the area (Uścinowicz et al. 1998).

Holocene deposits in the Gdańsk Basin include grey-brown and light grey clays of the Yoldia Sea and Ancylus Lake, which were deposited during Preboreal and Boreal times. Also the olive-grey, sometimes dark-grey or black, muds of the Litorina and Postlitorina seas, deposited during Atlantic, Subboreal and Subatlantic times. The average thickness of the Yoldia Sea and Ancylus Lake sediments is ca. 2-3 m, and of the overlying Litorina and Postlitorina sediments ca. 4-6 m (Ebbing et al. 2002).

MATERIALS AND METHODS

Field methods

The three cores used for this study (G11; G78; G82) were collected using a box core sampler in July 2006, during the cruise of the R/V IMOR. The cruise was organized by the Polish Geological Institute, branch of Marine Geology, and was a part of the project "Recognition and visualization of the geological settings of the Gulf of Gdańsk for the economy of mineral resources". The lengths of the three cores were approximately: G11, 25 cm; G78, 30 cm; G82, 35 cm. According to previously published sedimentation rates of this part of gulf (ca. 1.0-1.5 mm yr^{-1}) these lengths indicate about 200 to 350 years of sedimentation (Ebbing et al. 2002). Important considerations of studying such cores are bioturbation within the cores, and turbidity during sedimentation caused by near bottom currents. Two of the cores were cut into two pieces, while the third was kept whole. Details of the cores are outlined in Table 1.

Laboratory methods

The cores were washed on stainless steel sieves of <0.063 mm mesh size to remove the clay and mud fractions. Samples were then washed for five days in a 30% solution of H_2O_2 in order to dissolve the rest of the organic matter. The samples were then rewashed, to remove any traces of H_2O_2, and dried at 30°C.

Table 1

Core information.

Core number	G11	G78	G82
Date	July 2006	July 2006	July 2006
Latitude	54°29'48.85.08"	54°29'9.0539"	54°29'14.6853"
Longitude	18°55'21.9948"	19°01'49.6157"	19°06'30.8405"
Water depth	64.3 m	67.1 m	69.8 m
Core length	0.25 m	0.30 m	0.35 m
Diamiter of the core	0.08 m	0.08 m	0.08 m
Cores cutting	0-12; 12-25 cm	0-15; 15-35 cm	-

A strong magnet was used to collect the fine magnetic particles from the dried samples, and these were then studied using a stereo microscope (Carl Zeiss Stemi DV4/DR). Colour, transparency and glitter were recorded. Scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS) studies of the particles were undertaken at the "Didactic Laboratory of Scanning Microscopy" at Adam Mickiewicz University, Faculty of Geographical and Geological Science, using carbon-coated samples under a HITACHI S-3700N – High Technology microscopy. The EDS analyses were carried out on the surfaces of the spherules.

RESULTS

Two types of spherules were distinguished from the results of studies of their basic chemical composition and morphological features. External observations of spherule structure showed little difference between the two types. They are opaque black or dark gray and have a shiny, metallic luster. SEM revealed differences in details of size and surface characteristics, which were strongly supported by EDS studies.

Type 1 spherules range in diameter from 50 μm to 100 μm and have a regular, almost perfectly spherical shape, and one double form was seen (Fig. 2A). Their surfaces range from almost smooth with small holes (most having this form) to surfaces covered with bulbs growing from the main body (Fig. 2B and C). Delicate dendritic patterns were also seen (Fig. 2D and E). The internal structure of the spherules, visible on one that was partly damaged (Fig. 2F) has a "spongy" nature, probably having formed as a result of internal gases.

The chemical composition of type 1 forms is characterized by the domination of SiO_2 (up to 64%) and Al_2O_3 (up to 24%), with Fe_2O_3 also important in this group (see Table 2). The close back scattered electron image BSE (magnification ×4.5 k) revealed details of the structure, showing some

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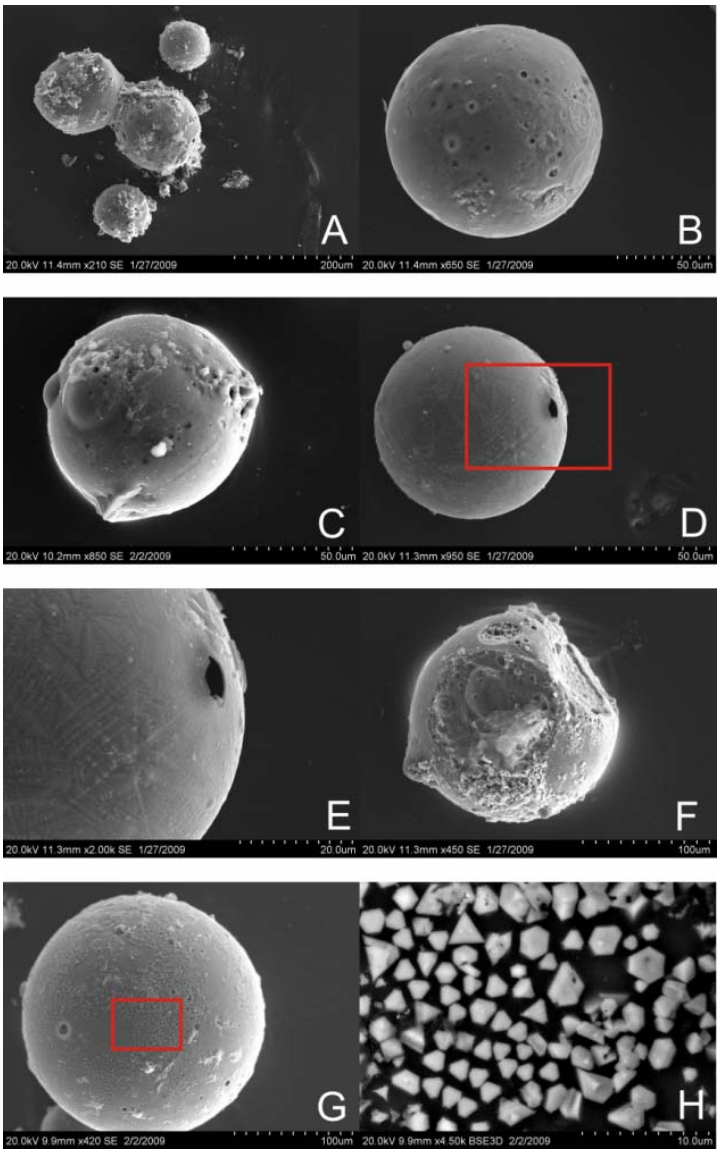


Fig. 2. Examples of anthropogenic spherules: A- double form; B- spherule with almost smooth surface with small holes; C- spherule with surface covered with bulbs growing from the main body; D and E- spherule with dendritic pattern (figure E shows the magnification of the marked area on the figure D); F- partly damaged spherule and the inner structure view; G- spherules composed of Fe-oxide crystals in glassy matrix; H- magnification of the marked area on figure G, in which the Fe-oxide crystals are clearly visible on the dark (silicate) background (BSE image).

spherules to be composed of Fe-oxide crystals in a glassy matrix (Fig. 2G and H).

Type 2 spherules are represented by two objects, with diameters of 50 μm and 75 μm. The surface of one of them is smooth with extensive fractures, possibly being evidence of a hollow space existing inside the spherule (Fig. 3A and B). On the surface of the second object the Widmanstaetten pattern was seen, and this spherule is also intriguing because it has a hole on its surface (Fig. 3C). This hole was probably created by escaping gases, and the edge of it is the starting point for a fracture that continues across its surface (Fig. 3D). This supports the idea that fractures are evidence of existing hollow spaces inside some spherules.

The chemical composition of type 2 spherules are entirely different from those in the first group; according to EDS analyses they are entirely composed of Fe_2O_3, with no other elements present (Table 2).

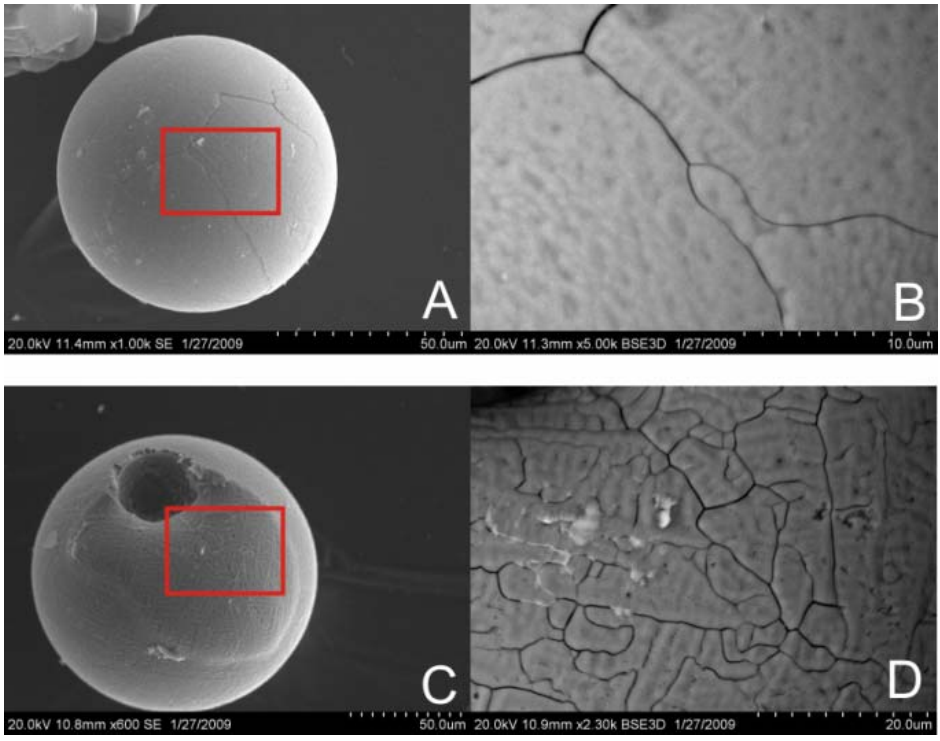


Fig. 3. Examples of extraterrestrial spherules: A and B- spherule with smooth surface (figure B shows the magnification of the marked area in figure A, with the extensive fracture is visible); C and D-spherule with Widmanstaetten patterns and the hole in the surface (figure D shows the magnification of the marked area on the figure C, starting area for the fracture is visible).

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Table 2

Average chemical composition of studied spherules [Wt %]. I-stands for spherules classified as anthropogenic; II-stands for spherules classified as extraterrestrial.

Sample number	Na_2O	MgO	Al_2O_3	SiO_2	Cl	K_2O	CaO	Cu_2O	Fe_2O_3	TiO_2	SO_3	V_2O_5	Ta_2O_5	MnO
G11 0-12 1 II	-	-	-	-	-	-	-	-	100.0	-	-	-	-	-
G11 0-12 2 I	3.5	1.2	22.5	47.8	-	-	13.1	-	9.6	2.2	-	-	-	-
G11 0-12 3 I	-	5.3	12.3	40.9	-	1.6	1.5	-	38.1	-	-	-	-	-
G11 12-24 1 I	4.3	1.2	14.7	32.9	0.7	2.4	10.7	-	33.0	-	-	-	-	-
G11 12-24 2 I	5.8		16.8	38.9	-	1.5	9.7	-	18.6	-	6.3	2.4	-	-
G11 12-24 4 I	1.7	1.7	9.4	64.5	-	3.2	6.7	-	12.8	-	-	-	-	-
G11 12-24 5 I			11.9	37.5	-	1.1	13.7	-	34.8	1.1	-	-	-	-
G78 0-15 1 II	-	-	-	-	-	-	-	-	100.0	-	-	-	-	-
G78 0-15 2 I	-	-	16.9	27.9	-	0.3	0.9	-	16.7	1.6	-	-	0.3	-
G78 15-30 1 I	2.4	1.5	17.8	37.4	-	0.7	4.9	-	34.1	1.3	-	-	-	-
G78 15-30 3 I	1.4	-	15.8	32.1	-	2.9	-	1.3	46.5	-	-	-	-	-
G78 15-30 4 I	2.7	1.3	24.7	37.8	-	1.3	1.9	-	29.5	-	-	-	-	0.8
G82 1 I	1.3	3.0	22.7	40.1	0.2	2.5	4.7	-	23.6	1.8	-	-	-	-
G82 2 I	2.3	2.6	24.0	46.3	-	2.4	7.7	-	13.4	1.3	-	-	-	-

DISCUSSION

Marine sediments, especially those near shore in the vicinity of industrial areas, are vulnerable to anthropogenic contamination, including industrial spherules. Nevertheless spherules of "natural" origin also occur (both from volcanic and extraterrestrial sources). Particles studied in this report include material representative of two numbers:

1. magnetic particles resulting from man-made activity
2. magnetic fines of extraterrestrial origin

The sources of magnetic, micro-scale grains in the Gulf of Gdańsk have not previously been considered in great detail. The chemical composition and external features of the particles, as well as their stratigraphic position, are important in determining their origins.

The spherules from the first group were classified as anthropogenic because their combination of chemical composition and regular shape are unprecedented in natural conditions. Such objects were previously described as being fly ash from coal-fired infrastructure (Puffer 1980, Blaha et al. 2008, Horng et al. 2009). The sample site from which they were obtained is located relatively close to the urbanized agglomeration of Gdańsk and Gdynia, so it would seem likely that they are man-made spherules from the coal-fired infrastructure in these cities, transported to the sea by the wind. These spherules were found throughout the whole core and, with a sedimentation rate in the area of ~1.0-1.5 m yr^{-1}, this indicates their deposition since the beginning of

industrial age in the 19th century. What is more in the late 1940's and 1950's the intensity of industrial activity in the area increased (Magiera 2004), causing noticeable pollution in the upper layers of local sediments (Magiera et al. 2006). However, more precise study methods are required in order to examine the cores with detailed time resolution.

The spherules from the second group are classified as extraterrestrial grains because of their homogeneous chemical composition and specific external patterns. Spherules of extraterrestrial origin are primarily formed as a result of ablation of meteoritic surfaces as they pass through the atmosphere (Shimanovich et al. 1995, Raukas 2004, Uścinowicz 2008a,b), their composition hence representing those of an iron meteorite. There are arguments that the presence of Ni in a sample is needed to classify such grains as extraterrestrial. This author believes that such small spherules (50 - 75 μm) could be free from this element, potentially due to weathering conditions or the migration of Ni during heating in the atmosphere (Raukas 2000, Marini et al. 2004, Stankowski et al. 2006). The Widmanstaetten patterns on the surface of the spherule also strongly supports the argument that their origin is cosmic; such patterns of kamacite and taenite with different crystal orientations are rather common in iron meteorites.

The mixture of spherical, magnetic grains in core samples is not uncommon; the growing activity of man and unstoppable natural processes, such as the constant influx of extraterrestrial matter to the Earth's surface, make the presence of such spherules in marine sediments rather probable (Uścinowicz 2008a).

CONCLUSIONS

Studies on marine core samples enabled several conclusions on the sources of magnetic spherules within them to be drawn:

- This investigation appears to be the first studying of magnetic fines in sediments of the Gulf of Gdańsk.
- Surface marine sediments are enriched in magnetic, micro-scale grains of different origin.
- The majority of the studied grains were classified as products of anthropogenic activity, and were primarily composed of SiO_2, Al_2O_3 and Fe_2O_3, with minor admixtures of other elements (Na_2O, MgO, CaO, K_2O, TiO_2). Such fly ashes are products of burning solid fuels, in this case probably originating from the cities of Gdańsk and Gdynia.
- Magnetic grains of extraterrestrial origin were also separated from core samples. Their composition is different to those from anthropogenic sources, comprising Fe-oxide, notably without any Ni content. Such

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spherules are postulated to originate as a result of ablation of meteoritic surface during their crossing through the atmosphere. Their composition represents the components of the "mother" meteoritic body, with the lack of Ni caused by weathering conditions or processes occurring during atmospheric entry.

- The sedimentation basin of an epicontinental sea, like the Gulf of Gdańsk, is not a dependable source of extraterrestrial spherules.
- The presence of anthropogenic dust in core samples is a record of pollution from nearby industrialized areas. The study of anthropogenic spherules could potentially be developed as a tool to determine sedimentation rates in marine sediments. However more precise studies are first needed to develop this method.

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