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RARE EARTH ELEMENTS IN Fe-Mn NODULES FROM THE SOUTHERN BALTIC SEA – A PRELIMINARY STUDY

PIERWIASTKI ZIEM RZADKICH W KONKRECJACH Fe-Mn Z POŁUDNIOWEGO BAŁTYKU – BADANIA WSTĘPNE

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Abstract. Between 1976–1990, the Polish Geological Institute performed geological works in the Polish Maritime Areas. During these works, 260 occurrences of concretions were recorded from 7,500 sampled sites. In 1980, the threshold that separates the Bornholm Basin from the Słupsk Furrow was mapped. Numerous Fe-Mn nodules on the seabed were found in that area. The results of detailed analyses of nodule samples collected from four sites are presented in this paper. Analyzed nodules represent discoidal D, irregular I, and transitional D-I types. The nodules are characterized by varied chemical composition of main oxides (Fe, Mn). The maximum Fe_2O_3 content is 26.63% and MnO 23.18%. Total average amount of REE + Y in the samples is approximately 165.11 ppm, ΣLREE 145.72 ppm and ΣHREE 19.39 ppm. The LREE content is enriched in comparison to HREE. The majority of nodules consist of Fe-Mn oxy-hydroxide minerals with very low crystallinity (practically amorphous phases). The main confirmed Mn-phases are birnessite and todorokite. Other main components of the nodules are: detrital quartz, albite, microcline, glauconite and muscovite, clinochlore, and clay minerals: illite and chlorite. The rate of growth of Fe-Mn nodules has been estimated using a cobalt chronometer. The nodule growth rate ranges from 0.006 to 0.134 mm/yr $^{-1}$. Based on the Fe, Mn and (Cu + Co + Ni) contents, the origin of studied nodules is determined as hydrogenetic, while using REE (Ce_{sn}/Ce_{sn} · vs. Nd) – as diagenetic.

Key words: Fe-Mn nodules, Baltic Sea, REE.

Abstrakt. W latach 1976–1990 Państwowy Instytut Geologiczny realizował prace geologiczne na Polskich Obszarach Morskich. Opróbowano 7500 miejsc, a w 260 stwierdzono występowanie konkrecji. W roku 1980 prace kartograficzne prowadzono m.in. na obszarze progu oddzielającego Basen Bornholmski od Rynny Słupskiej, gdzie stwierdzono występowanie licznych konkrecji Fe-Mn. W niniejszym artykule są prezentowane wyniki analiz konkrecji pobranych na 4 stanowiskach. Badania dotyczą konkrecji następujących typów: dyskoidalnych D, nieregularnych I oraz przejściowych D-I. Badane konkrecje charakteryzują się zmiennym składem głównych tlenków (Fe, Mn). Maksymalna zawartość Fe_2O_3 wynosi 26,63%, a MnO 23,18%. Łączna średnia zawartość REE + Y w badanych próbkach jest na poziomie 165,11 ppm, ΣLREE – 145,72 ppm i ΣHREE – 19,39 ppm. Zauważalne jest wzbogacenie w LREE w porównaniu do HREE. Konkrecje w większości są zbudowane z tlenków i wodorotlenków Fe i Mn o bardzo niskim stopniu krystaliczności (praktycznie fazy mineralne są amorficzne). Głównymi potwierdzonymi fazami manganu są birnessyt i todorokit. Pozostałymi głównymi składnikami konkrecji są: kwarc terygeniczny, albit, mikroklin, glaukonit i muskowit, klinochlor, minerały ilaste: illit, chloryt. Wartość tempa wzrostu w badanych konkrecjach, określona z użyciem chronometru kobaltowego, wynosi od 0,006 do 0,134 mm/yr $^{-1}$. Na podstawie zawartości Fe, Mn oraz (Cu + Co + Ni) badane konkrecje określono jako hydrogeniczne, podczas gdy używając zależności REE (Ce_{sn}/Ce_{sn} · vs. Nd) jako diagenetyczne.

Słowa kluczowe: konkrecje Fe-Mn, Bałtyk, REE.

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INTRODUCTION

Fe-Mn nodules (concretions) have been identified in all oceans and many seas. The first stage of the nodule studies was focused on the origin of the mineral substances building nodules, their origin, the character of diagenetic processes, the chemical and mineral composition, as well as the potential of metals present in the nodules (Mero, 1965; Bonatti *et al.*, 1972; Glasby, 1977; Kotliński, Szamałek, 1998; Kotliński, 1999). The nodules contain significant amounts of valuable metals (Ni, Co, Cu). The enrichment of metals in nodules is caused by acquiring metals from seawater (hydrogenetic), as well as pore fluids (diagenetic). The majority of investigated nodules have a mixed origin, primarily either hydrogenetic-diagenetic or hydrothermal-hydrogenetic (Hein *et al.*, 1997; Baturin *et al.*, 2014; González *et al.*, 2016). The mainstream international researches have been concentrated on the nodules occurring at the deep ocean floor, especially in the Pacific Ocean – Clarion-Clipperton Zone (CCZ). However, the nodule resources in the Russian sector of the Gulf of Finland are well-documented and even were experimentally mined (Ryabchuk *et al.*, 2017). Deep-ocean nodules are strongly enriched also in other metals, such as Mo, Zr, Li, Y and REEs (Hein *et al.*, 2013), therefore they are currently considered as a potential source of REE. There are numerous contributions dedicated to the distribution and mineralogy of the Baltic Sea nodules (Winterhalter, 1980; Piper, 1974; overview given by Baturin, 2009), but the REE content in the Baltic nodules was the subject of only a couple of publications. The riverine input of REE into the Baltic Sea was studied by Ingri *et al.* (2000). Next researches were focused on the distribution of REE in bottom sediments of the Baltic Sea (Emelyanov *et al.*, 2002; Kunzendorf, Vallius, 2004). The nodules from shallow epicontinental seas and freshwater lakes have been investigated less frequently (Lysuk, Lysuk, 2009). The Fe-Mn nodules coming from shallow-water zones of the Baltic Sea are relatively fast growing, which facilitates spatial, and hence, temporal resolution of their geochemical record (Hlawatsch *et al.*, 2002a). The growth rate of ferro-manganese nodules from the western Baltic Sea was determined as 0.02 ±0.002 mm/yr^{-1} (Hlawatsch *et al.*, 2002b). The comparative analysis of nodules from the Gulf of Cadiz and the Baltic Sea is presented by González *et al.* (2010). Researches of shallow shelf sediments (including nodules) indicated that they can be a source of REE (Pourret, Tuduri, 2017). They suggested that the Atlantic continental shelf could be considered as potential REE traps and shelf sediments would represent, like metalliferous deep-sea sediments, a potential REE resource. Kuhn *et al.* (2017) estimated that one nodule mining project in the CCZ zone could deliver 12 kt REO annually. Therefore, current international investigations are concentrated on Fe-Mn nodules as the potential sources of REE. Additionally, the growing demand of the world economy for REE is the reason why the extension of the scope of research of the shallow Baltic nodules as a potential source of REE is proposed.

Data on the distribution and composition of Fe-Mn nodules in the Baltic Sea were published mainly in the second half of the 20th century (*e.g.* Manheim, 1961, 1965; Winterhalter, 1966, 1980; Winterhalter, Siivola, 1967; Varentsow, Blashchishin, 1976; Calvert, Price, 1977; Suess, Djafari, 1977; Ghiorse, 1980; Winterhalter *et al.*, 1981; Bostrom *et al.*, 1982; Ingri, Ponter, 1986, 1987; Heuser, 1988; Moenke-Blankenburg *et al.*, 1989; Lass, Matthaus, 2008). There are also contributions published in the Polish language (Pęcherzewski, 1973; Kulesza-Owsikowska, 1979, 1981; Osadczuk, 1991; Szefer *at al.*, 1998, 1999; Szefer, 2002). The last papers summarizing the knowledge on Fe-Mn nodules from the Polish part of the Baltic Sea come from 1996 and 1998 (Glasby *et al.*, 1996, 1997; Trokowicz, 1998).

There are three main types of nodules occurring in the Baltic Sea: spheroidal, discoidal and crusts (Glasby *et al.*, 1997). The Mn and Fe content in nodules varies from 8 to 30% and from 10 to 23%, respectively, and depends on both the nodule type and the region of occurrence. The nodules from Bothnian Bay and the eastern Gulf of Finland are most abundant, with the abundance reaching in places 40 kg/m^2. Within the Russian sector of the Gulf of Finland, the average abundance of spheroidal concretions is about 20–30 kg/m^2, reaching in some places 50 kg/m^2 (Zhamoida *et al.*, 2007). These concretions are mostly spheroidal, up to 30 mm in diameter, the Mn/Fe ratio is determined as 0.68–0.88, and they are associated with muddy, organic-rich sediments adjacent to depressions. Concretions in the Bothnian Sea, central Gulf of Finland and Gulf of Riga are common to abundant (15–18 kg/m^2). In Bothnian Bay, the nodules like to flat crusts are widely distributed, whereas in the Gulf of Riga, spheroidal and discoidal concretions occur (Mn/Fe ratio around 0.43). The nodules in the central and southern Baltic Sea are found mainly around the margins of the deep basins and on sills separating them. The shape of nodules is mainly discoidal (20–150 mm in diameter) and the Mn/Fe ratio is about 0.5–0.6. Their abundance is sporadic to common; only locally reaching 10–16 kg/m^2. In the western Baltic Sea, the concretions are known from Kiel, Lübeck and Mecklemburg bays and are spheroidal with a diameter of 10–30 mm and discoidal with a diameter of 20–100 mm. The Mn/Fe ratio of the Baltic concretions varies from 2.6 to 2.9 (Glasby *et al.*, 1997; Uścinowicz *et al.*, 2011; Uścinowicz, 2014).

The present knowledge on the distribution and morphology of ferromanganese concretions in the Polish Maritime Areas comes from the geological mapping programme carried out by the Polish Geological Institute (PGI) during the years 1976–1990. In the framework of this programme, about 260 occurrences of concretions were recorded (Fig. 1) from 7,500 sampled sites. In that period, detailed investigations of nodules were not undertaken. Therefore, there is no detailed knowledge on the quantity, morphology, mineralogy and composition of ferromanganese concretions from the Polish part of the Baltic Sea, especially about REE contents.

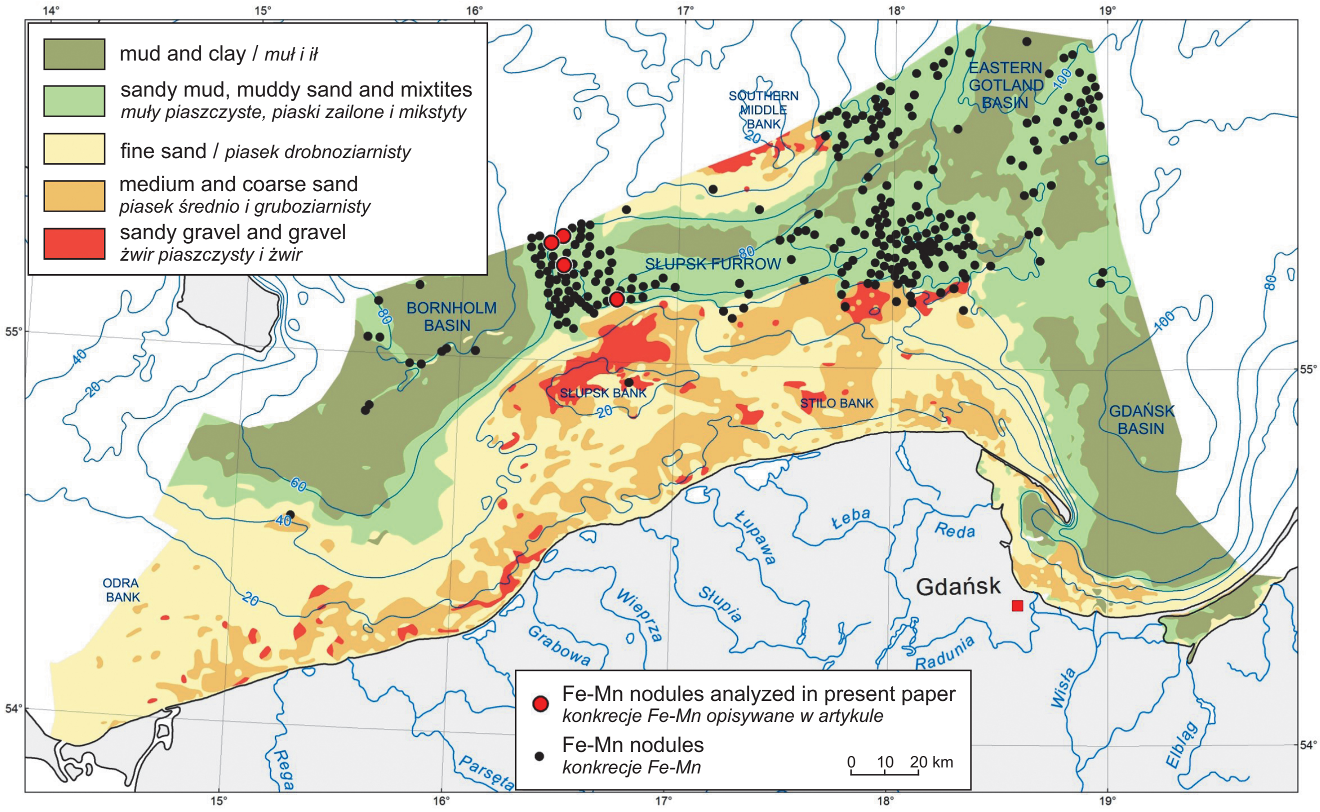

Fig. 1. Location of nodule samples on the *Geological Map of the Baltic Sea Bottom*, 1 : 200,000 (after Mojski 1989–1993, simplified)

Lokalizacja próbek konkrecji na tle *Mapy Geologicznej Dna Morza Bałtyckiego* w skali 1 : 200 000 (wg Mojskiego 1989–1993, uproszczona)

GEOLOGICAL SETTING OF THE INVESTIGATED AREA

The Baltic Sea is a shallow, young (the age *ca*. 15–14 kyrs) intracontinental sea with an average depth about 50 m. The sea bottom reveals numerous basins and depths separated by elevations and thresholds (Fig. 1).

The Polish Maritime Areas comprise the eastern part of the Bornholm Basin, Słupsk Furrow, western part of the Gdańsk Basin, and southern peripherals of the Eastern Gotland Basin. In the Polish part of the Baltic Sea, between the coast and the slopes of deep-water basins, the seabed descends gently to a depth of approximately 30–40. In this shallow seabed area there are three seabed elevations (banks) recognized: Odra Bank, Słupsk Bank and Stilo Bank.

Recent sediments in the southern Baltic Sea are the result of multiple redeposition of eroded Pleistocene glacial and glaciofluvial deposits. Boulders and cobbels are found most often on the NW part of the Słupsk Bank and in the near-shore zone close to the cliff coast. Gravels, sandy gravels and gravelly sands occur mostly in the depth zone of 10–30 m, in the form of irregular fields, often adjacent to the areas of boulders. Coarse and medium sands are common in the depth zone of 10–25 m. Fine sand is the most common type, dominates in the depth zones between 0–10 and 25–55 m, and also occur in small, irregular patches associated with coarser sediments. Muds, enriched by organic matter, are most widespread in the Bornholm and Gdańsk basins and are less common in the Słupsk Furrow and the southern periphery of the Eastern Gotland Basin (Fig. 1).

In the transition zone between muddy sediments and sand, on the peripheries of deep-water sedimentary basins and on sills separating them, occur sandy-silty sediments or mixtites, *i.e.* sandy-gravelly-silty sediments. These sediments most often occur in the bottom areas where the halocline is in contact with the seabed. They are poorly and very poorly sorted. The thickness of sandy-silty sediments and mixtites is often less than 0.2 m, in places below 0.1 m. The sandy-silty sediments are underlain by clays of the early phases of Baltic Sea development and the mixtites are underlain by clayey till deposited during subaqueous deglaciation of the Baltic area. These sediments contain about 1.5–2.0% of organic matter. Ferromanganese nodules are associated very often with these types of sediments. Lithologic features and sonar images of the seabed from the areas of occurrence of sandy-silty sediments and mixtites indicate that the sedimentary regime in this area is very dynamic (Uścinowicz, 2014).

Ferromanganese concretions commonly occur on the thresholds between the Bornholm Basin and Słupsk Furrow, and between the Słupsk Furrow and Gdańsk Basin, as well as on the western and eastern edges of the southern part of the Eastern Gotland Basin (Fig. 1). The nodules occur mainly as discoidal and more rarely as irregular crusts.

SAMPLING AND METHODS OF INVESTIGATION

FIELD WORK

During the years 1976–1990, the Polish Geological Institute executed geological operations in the Polish Maritime Area for the preparation of the *Geological Map of the Baltic Sea Bottom at the scale 1 : 200,000* (Mojski, 1989–1993). In 1980, geological mapping was performed in the threshold that separates the Bornholm Basin from Słupsk Furrow. In this region, numerous Fe-Mn nodules were identified on the seabed (Kramarska, 1991). Samples of nodule-containing seabed sediments were collected using a Van Veen grab sampler, which covers a seabed area of 0.35 × 0.4 m (0.14 m^2). The bulk samples contained nodules of discoidal D, irregular I, and transitional D-I morphological types. The geographical coordinates of the samples (Tab. 1; Fig. 1) were determined using the DECCA system (accuracy ±100 m). The nodules were separated from the sediment and were stored in plastic bags at room temperature (weight of the nodule samples (g): 102H – 51.33; 107H – 126.13; 113H – 94.73; 131H – 65.18).

ANALYTICAL METHODS

Thin-sections of nodules were prepared for microscopic investigations (NIKON ECLIPSE E600 POL microscope). The microscope observations were performed using polarized light (reflected and transmitted; LU Plan Fluor lenses from ×2.5 to ×50). The microscope observations were supplemented by a photo documentation (camera Nikon DS. – 5 Mc, resolution 5 million pixels) using the NIS Elements Program.

The internal structure of nodules was observed using a scanning microscope (SEM) ΣIGMA VP with two detectors EDS (SDD XFlash | 10) made by Bruker Company. Detailed studies of microstructure and forms of Fe-Mn phases, as well as elements mapping were performed. SEM investigations were carried out on carbon film samples using high vacuum conditions. An accelerating voltage of 20 kV.

The mineral composition analysis was carried out by X-ray diffraction in the Bragg-Brentano system on a Bruker-AXS D8 diffractometer DAVINCI equipped with a lamp with a copper anode. Diffractograms were recorded in the angular range from 3 to 70° 2θ (Cu Kα), measuring step 0.019°, and counting time 6 s/step. The optical system consists of primary slit 0.3°, secondary slit 1.5°, soller slit 2.5°, a Ni Kβ filter and a LynxEye PSD detector. Crystalline phases were identified by comparing the registered diffractograms with the patterns found in the ICDD PDF-2 and PDF-4 + 2016 database using the DIFFRACplus EVA-SEARCH program.

Electron microprobe analyses (EMPA) were performed at the Inter-Institute Analytical Complex for Minerals and Synthetic Substances of the University of Warsaw with a CAMECA SX-100 electron microprobe operating in wavelength dispersive (WDS) mode. On spectrometers equipped with crystals (TAP, LIF, PET, LPET), spectra of particular elements were studied. Operating conditions include an accelerating voltage of 20 kV, beam current 15 nA, beam diameter around 2 μm, peak count time 20 s, and background time 10 s. The limit of detection, standards and standard deviation are presented in Appendix 1[3]. Due to the high porosity of nodules, the total sum of chemical analyses is not 100%.

Research on the chemical composition of concretions was carried out in the ACME Labs certified laboratory in Vancouver (Canada). A representative part of the samples was dried at 105–110°C, then hand-pulverized in mortar and pestle. The samples were averaged. To determine the contents of oxides and rare earth elements, the analytical programs LF200 and MA270 (www.acmelab.com) were used. The solutions were analyzed using the ICP-ES and MS methods. The C and S contents were determined using the LECO organic analyzers. In this study, we used $Ce/Ce^* = 2Ce_{sn}/(La_{sn} + Pr_{sn})$, $Ce_{anomaly} = \log(Ce_{sn}/Ce^*_{sn})$, $Eu_{sn}/Eu^* = 2Eu_{sn}/(Sm_{sn} + Gd_{sn})$, where sn refers to normalization of concentration against the Post-Archean Australian shale composite (PAAS; McLennan, 1989). Discrimination plots used PAAS normalized REE + Y data with

Table 1

Location and description of nodule samples

Lokalizacja i opis próbek konkrecji

Sample No.	Coordinates		Water depth [m]	Sample description
	ϕ	λ		
102H	55°15'14.7"	16°27'58.8"	59.0	Thin layer (*ca*. 2 cm) of poorly sorted sand with gravel and numerous Fe-Mn nodules on clayey till
107H	55°18'44.7"	16°24'10.9"	61.5	Thin layer (*ca*. 2 cm) of poorly sorted silty sand with numerous Fe-Mn concretions on clayey till
113H	55°10'02.7"	16°43'04.9"	72.5	Thin layer (*ca*. 2 cm) of poorly sorted sand with a few Fe-Mn concretions on clayey till
131H	55°19'50.7"	16°27'28.9"	57.5	Thin layer (*ca*. 5 cm) of poorly sorted sand (78%) with admixture of gravel (13.1%), slightly silty with Fe-Mn concretions on clayey till

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[3] Appendix can be found in the online version of this article (https://biuletynpig.pl).

$Ce_{sn}^{*} = 0.5La_{sn} + 0.5Pr_{sn}$, plots are $Ce_{sn}/Ce_{sn}\cdot$ vs Nd (Bau *et al.*, 2014). The growth rate of Fe-Mn nodules was calculated using the empirically derived cobalt chronometer proposed by Manheim and Lane-Bostwick (1988): $(GR) = 0.68/(Co_n)^{1.67}$, where: $Co_n = Co \times (50/Fe + Mn)$ with Co, Fe and Mn expressed as weight percent (wt%).

RESULTS

STRUCTURE AND MORPHOLOGY

All the examined Fe-Mn nodules are characterized by varied sizes (from 2 to 8 cm in diameter) and morphologies (Fig. 2), and represent three types:

Type D – brownish-rusty to black-brownish discoidal nodules (8 cm in diameter), with irregular and rough surface without macroscopically visible concentric layers (Fig. 2A).

Type I – brownish-rusty rings on the surface of granite pebbles. The width of rings varies from a few mm to 1 cm. The diameter of granite pebbles varies from 2 to 4 cm (Fig. 2B).

Type D-I – rusty to brownish transitional nodules (diameter up to 3 cm) with an internal hollow and well-rounded augmentative margins (Fig. 2C).

MINERALOGY

The diffractograms (Fig. 3) show strong overlaps and low crystallinity of the oxy-hydroxide minerals. The main Mn phases are birnessite and todorokite, but the samples also contain undefined Fe and Mn phases (goethite?, vernadite?). Other main components of the nodules are: detrital quartz, albite, microcline, glauconite and muscovite, clinochlore, clay minerals: illite, chlorite.

Detailed observation revealed the presence of the zone of red-brownish Fe-oxides and Fe-hydroxides, black zone of Mn-oxides and hydroxides, as well as terrigenous components. Additionally, the element distribution in different zones of nodules was studied (Figs. 4–5). It is possible to recognize the separate layers of Fe and Mn minerals. The positive optical correlation between Fe and Co is visible (Figs. 4–5).

Type D nodules have a complex structure composed of a heterogeneous internal zone and a concentric-layered external zone. Their mineralogical composition contains quartz, plagioclases and single barite, altered brownish glauconite and a small amount of heavy minerals represented by ilmenite and zircon. Quartz occurs as crystals 0.1–0.5 mm and dominates in the internal zone. The quartz grains are modrately to poorly rounded and mostly semi sharp-edged. Plagioclases occur as moderately rounded tablets up to 0.15 mm. Barite grains (up to 0.8 mm) are well-rounded. Heavy minerals occur as fine-grained grains up to 0.1 mm. Spindle-shaped grains are rare.

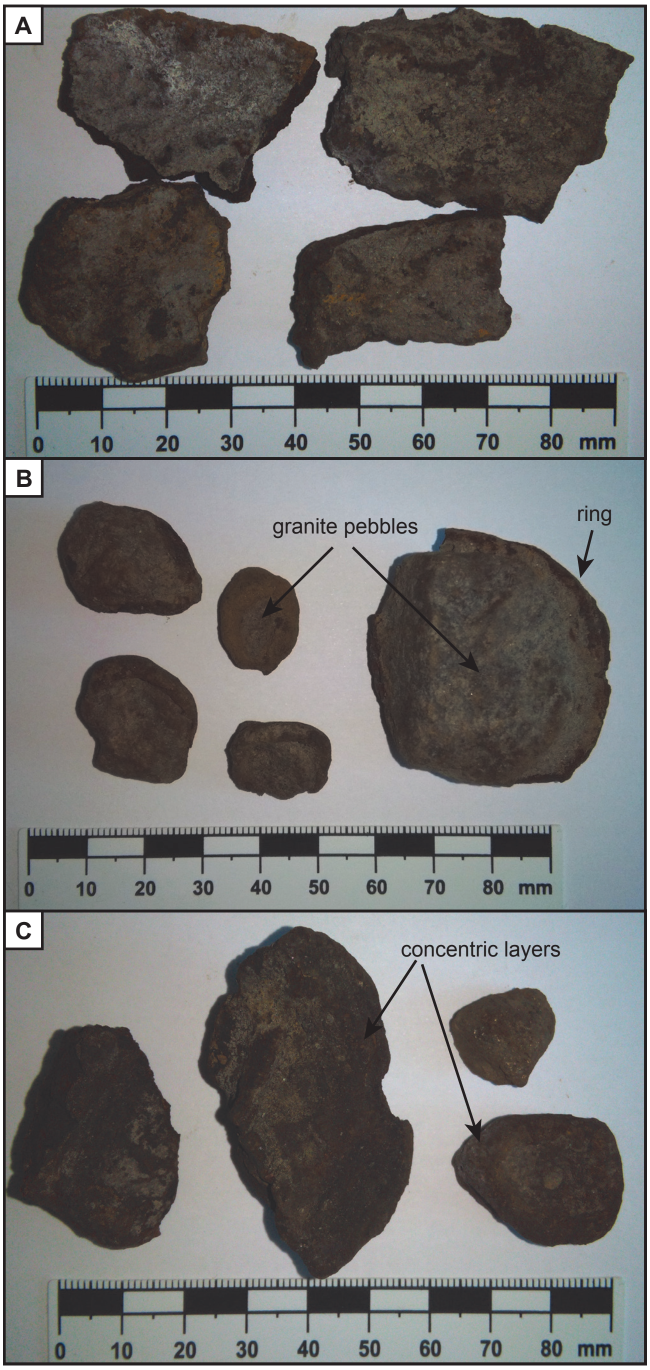

Fig. 2. Nodules sampled from the southern Baltic Sea: A – discoidal (fragments), B – irregular, C– transitional

Konkrecje pobrane z dna południowego Bałtyku: **A** – dyskoidalne (fragmenty), **B** – nieregularne, **C** – przejściowe

The Fe-Mn zone in **type I nodules** (Fig. 5) has a concentric-layered structure composed of irregular red-brownish and black laminae. Terrigenous components of the aleuritic-psammitic fraction dominate in the Fe zone. The Fe-layers are composed of heterogeneous amorphic mass. The laminae are up to 2.5 mm in width. The Mn-zone is present as a layered-collomorphic structure with outgrowths of fine-grained laminae. The Mn layers are up to 1.5 mm in size. The nodules have high porosity. Terrigenous components occur randomly and consist of quartz, albite, microcline, altered brown glauconite, chlorite, zircon, ilmenite and fragments of rocks (composed from quartz, plagioclases and biotite).

Quartz occurs as two populations differentiated by size and shape: a) elongated grains, irregular, poorly rounded, up to 0.65 mm, b) discoidal and ellipsoidal grains well- and very well-rounded, up to 0.1 mm. The plagioclases and K-feldspars occur as single poorly rounded tablets up to 0.4 mm, and altered by the sericitization processes. The microcline lattice shows twinning and pertite symphisis. Glauconite consists of large brownish altered crystals up to 0.8 mm.

Type D-I nodules consist of two zones differing in mineral composition and internal structure. Central part of the nodule is composed of the psammitic skeleton (up to 0.25 mm) and the aleuritic matrix with lesser amounts of quartz grains and plagioclases. The heavy minerals contain single grains of ilmenite, rutile, zircon and monazite. The matrix is composed of very fine-grained ferruginous silica with numerous manganese traces. The outer zone consists of the

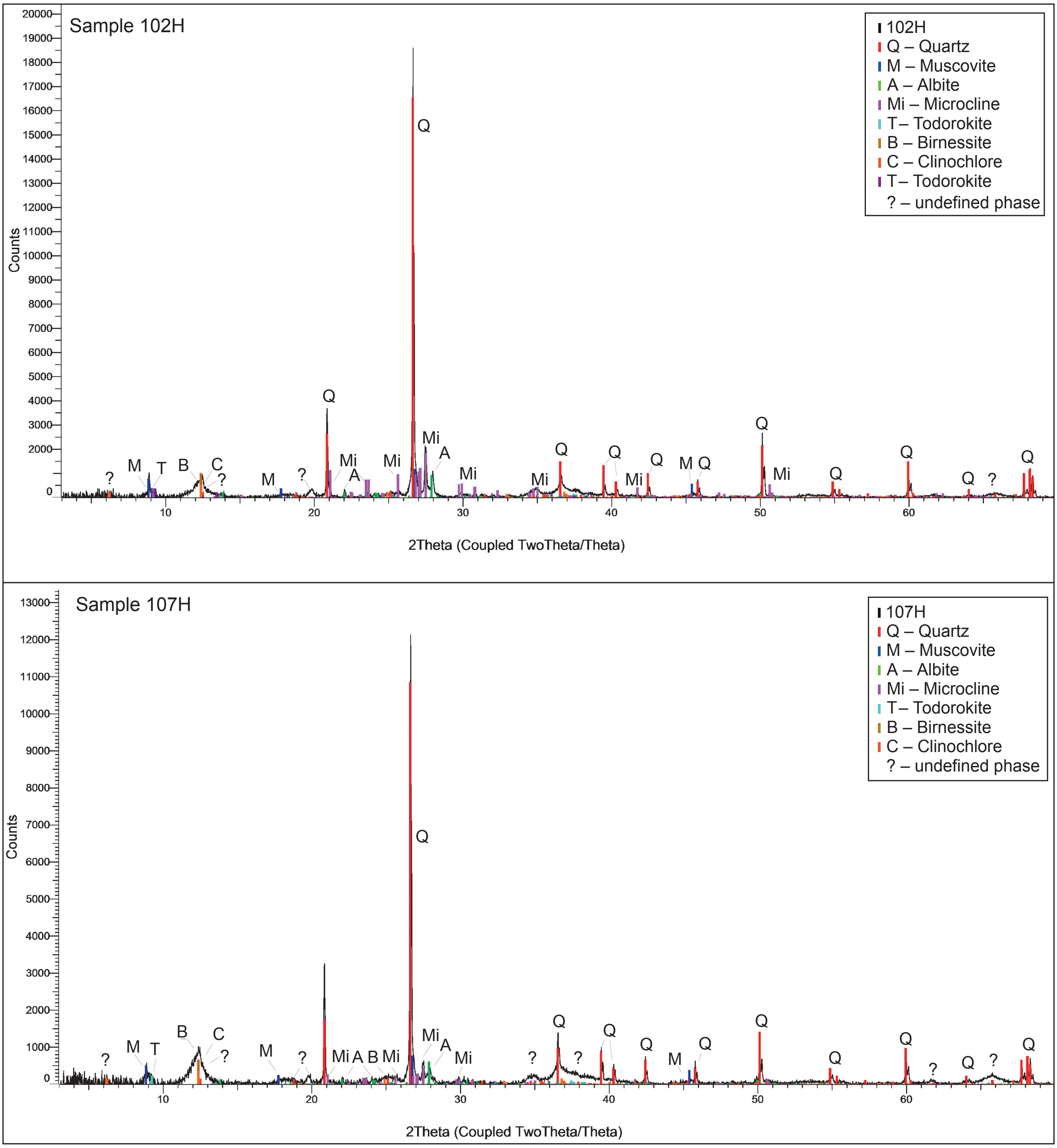

Fig. 3. Diffractograms of bulk nodule samples

Dyfraktogramy próbek konkrecji

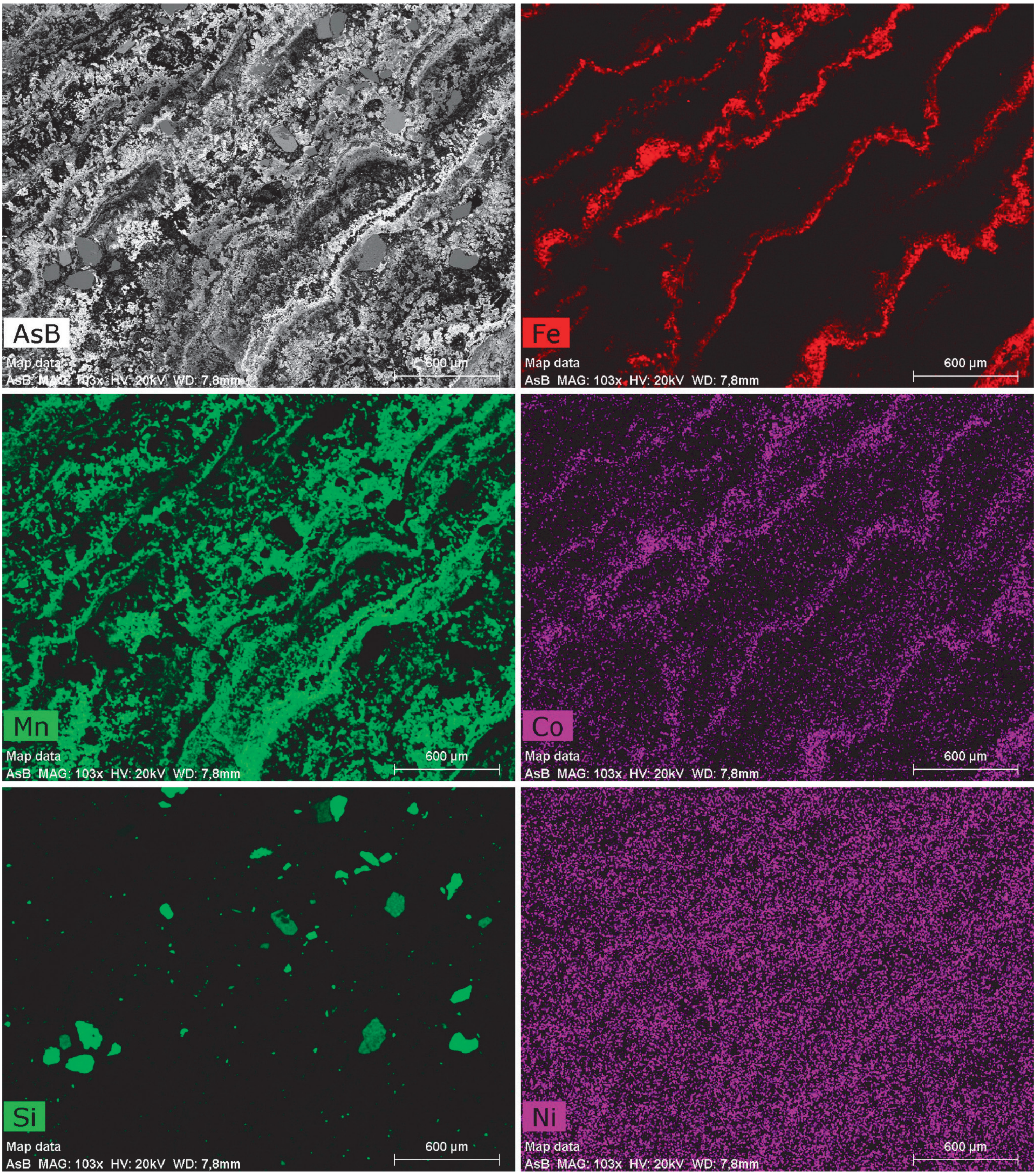

Fig. 4. The distribution of elements in a transitional nodule – sample 107H type D-I (SEM-BSE)

Rozkład pierwiastków w konkrecji typu przejściowego – próbka 107H typ D-I (SEM-BSE)

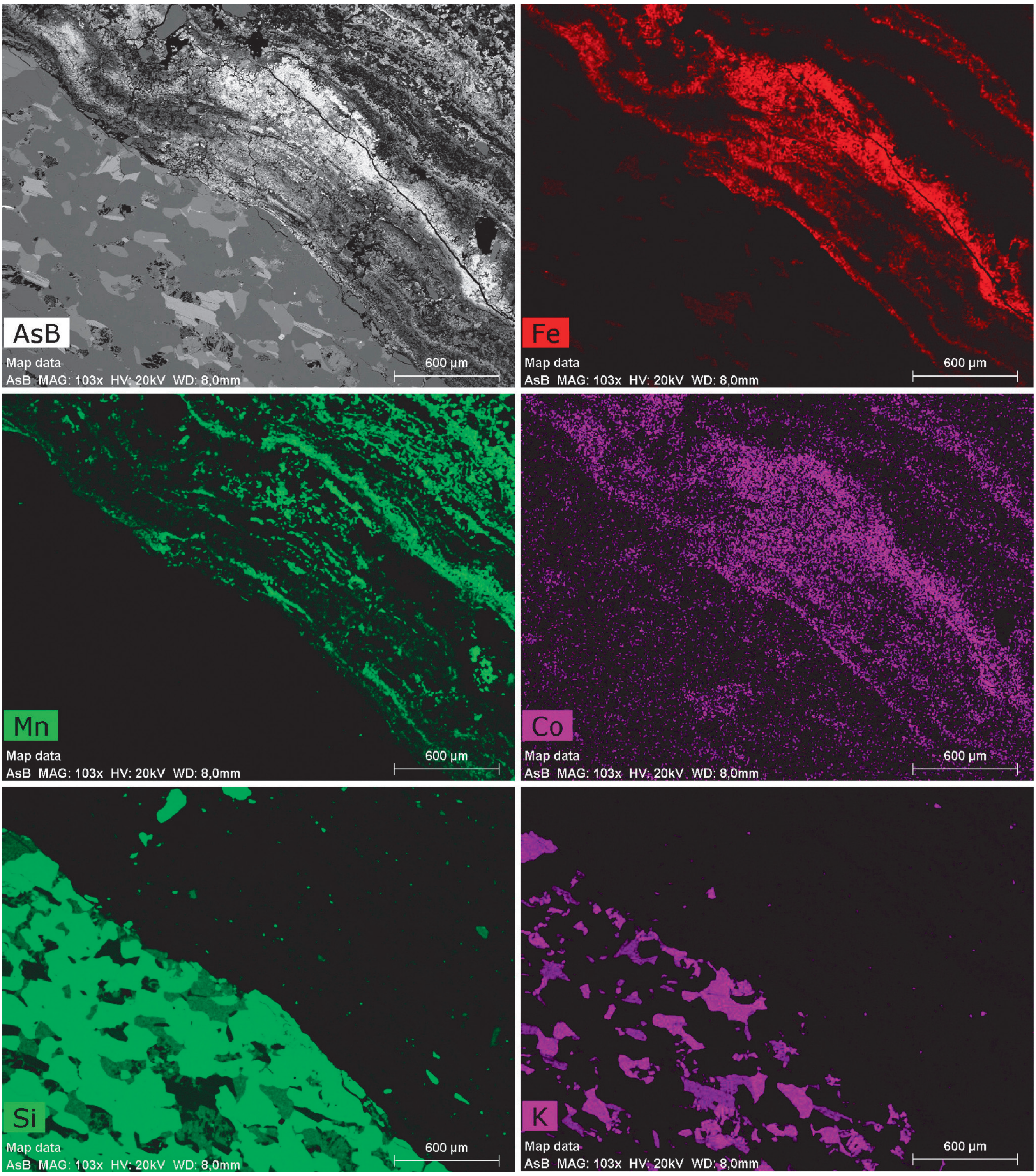

Fig. 5. The distribution of elements in a nodule of irregular type – sample 131H type I (SEM-BSE)

Rozkład pierwiastków w konkrecji nieregularnej – próbka 131H typ I (SEM-BSE)

Fe-Mn mass showing a layered-collomorphic structure. The widths of Mn and Fe laminae are up to 0.2 mm and up to 0.3 mm, respectively. The Mn laminae are separated by irregular Fe laminae. Psammitic grains of terrigenous components are less frequent than aleuritic ones. Quartz is the dominant mineral in the Fe layer, plagioclase (up to 0.2 mm in size) is less abundant, green glauconite (up to 0.2 mm) occurs sporadically. There are also single grains of altered biotite and very fine-grained heavy minerals (up to 0.1 mm). In the Mn zone, quartz is rare and occurs as very fined-grained grains (up to 0.45 mm). The mineral grains are moderately to well-rounded. Plagioclases are present as very fine-grained grains altered during the sericitization processes.

GEOCHEMISTRY

Based on the EPMA analysis it is possible to distinguish the diversity of chemical composition of each individual laminae (Tab. 2). The red-brownish laminae contain from 51.23[4] to 73.53% Fe_2O_3, and up to 0.68% MnO. In the transitional zone the maximal content of Fe_2O_3 is up to 51.23%, MnO up to 31.89%. The black laminae contain 56.87–67.51% MnO, and 0.12–3.34% Fe_2O_3. The ferruginous laminae are characterized by higher contents of some chemical components than the manganese ones (CaO up to 3.74%, P_2O_5 up to 12.52%, SiO_2 up to 7.44%). In contrast, the Mn laminae have higher contents of MgO (up to 4.39%) and K_2O (up to 1.85%).

The analyzed nodules are characterized by varied chemical composition of main oxides (Fe, Mn; Tab. 3). The maximum Fe_2O_3 contents are 26.63%, MnO 23.18%. The Fe/Mn ratio ranges from 0.21 to 1.36. Thus, the nodules are of hydrogenetic origin. There is a negative correlation between Fe and Mn. The contents of the remaining main chemical components are as follows: SiO_2 25.84–50.74%, average 36.76%; Al_2O_3 4.40–11.06%, average 7.43%; K_2O up to 2.46%. The higher Al_2O_3 content indicates the presence of clay minerals, especially in the internal zones of discoidal and spherical nodules. The average content of CaO is 1.13%, Na_2O 1.15%, P_2O_5 1.68%. The presence of phosphorus is probably related to P-minerals in the layers enriched in Fe. TiO_2 and Cr_2O_3 are present at the percentages of 0.38 and 0.009%, respectively. The TOT/C content varies from 0.81 to 1.12%, while the TOT/S from 0.03 to 0.06%. LOI (loss of ignition) ranges between 10.4 and 18.4%.

The total amount of Cu + Ni + Co is low and varies from 184.5 to 470.4 ppm. Small amounts of Zn, V and Pb are also present. In contrast, the contents of Ba, Sr and Li are the highest due to the presence of K-feldspar and plagioclases, as well as terrigenous and/or authigenic Ba sulphate.

The growth rate (GR) of the nodules varies from 0.006 to 0.134 mm/yr^{-1}. The growth rate of nodules from the economic marine zone of Poland was estimated as 0.013–0.018 mm/yr^{-1} (Glasby *et al.*, 1997). Anufriev and Boltenkov (2007) determined the GR of Baltic nodules from the Gulf of Finland by the space tracer method based on the ^{3}He stable isotope supplied to sediments by cosmic dust. In conclusion, they indicated than the GR in the Gulf of Finland is 8–9 mm/yr^{-1}. This result is compatible with data determined by Hlawatsch *et al.* (2002b) for nodules from the Gulf of Finland, but is significantly different from the GR of nodules from the western Baltic Sea (20 mm/yr^{-1}). Anufriev and Boltenkov (2007) criticized the last result and argued that it cannot be considered as reliable for methodological reasons.

The origin of studied nodules was determined based on their chemical composition (Fig. 6). They represent hydrogenetic (Fig. 6) or to diagenetic (Fig. 7) nodules according to the REE composition. For a conclusion about the origin of the nodules it is necessary to perform detailed examinations of Mn phases using IR and XPS methods.

Table 2

Distribution of chemical components in different zones of nodule (sample 102H) [wt%]

Rozmieszczenie składników chemicznych w różnych strefach konkrecji (próbka 102H) [wt%]

Oxides	Mn-zone			Transition Fe-Mn zone		Fe-zone		
	1	2	3	4	5	6	7	8
SiO_2	0.81	0.36	0.13	4.89	2.23	7.10	4.47	7.44
TiO_2	0.00	0.02	0.03	0.00	0.02	0.01	0.03	0.01
Al_2O_3	0.35	0.17	0.05	0.79	0.38	1.82	0.01	0.96
Fe_2O_3	0.35	0.47	2.8	51.23	31.20	67.73	66.13	64.88
P_2O_5	0.10	0.15	0.25	3.16	2.18	8.83	12.52	8.84
MgO	3.63	2.60	2.45	1.19	1.97	1.40	1.51	1.64
CaO	1.66	2.00	1.72	2.73	2.50	2.89	3.74	3.11
MnO	6.21	65.49	62.14	20.71	31.89	0.68	0.08	0.95
Na_2O	1.80	2.97	1.87	0.37	0.71	0.90	1.75	1.79
K_2O	1.48	1.28	1.14	0.35	0.57	0.63	0.38	0.40
Cl	0.12	0.09	0.06	0.36	0.76	0.06	0.09	0.26
Total	**75.54**	**72.27**	**72.69**	**85.83**	**74.46**	**92.09**	**90.76**	**90.30**

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[4] All geochemical data are in weight percent [wt%].

Table 3

Chemical composition of nodules

Skład chemiczny konkrecji

Oxide/Element	Unit	Sample 131H	Sample 107H	Sample 102H	Sample 113H	Average
SiO_2	%	50.74	25.84	33.88	36.61	36.76
Al_2O_3	%	11.06	4.40	5.95	8.31	7.43
Fe_2O_3	%	12.74	18.80	19.35	26.63	19.38
MgO	%	2.14	1.93	1.87	2.23	2.04
CaO	%	0.95	1.39	1.18	1.00	1.13
Na_2O	%	1.16	1.40	1.11	0.94	1.15
K_2O	%	3.37	1.90	2.16	2.41	2.46
TiO_2	%	0.58	0.23	0.33	0.41	0.38
P_2O_5	%	0.84	1.98	1.77	2.13	1.68
MnO	%	5.74	23.18	16.24	5.24	12.6
Cr_2O_3	%	0.010	0.009	0.010	0.010	0.009
LOI	%	10.4	18.4	15.7	13.7	14.55
Total	**%**	**99.81**	**99.74**	**99.78**	**99.77**	**99.77**
TOT/C	%	0.81	1.12	0.91	1.16	1
TOT/S	%	0.04	0.06	0.04	0.03	0.04
Ba	ppm	758	2197	2130	1008	1523.25
Ni	ppm	114	306	216	130	191.50
Sc	ppm	10	4	5	8	6.75
Be	ppm	2	<1	2	3	2.33
Co	ppm	40.4	121.2	135.8	104.0	100.35
Cs	ppm	4.1	1.6	2.0	3.0	2.67
Ga	ppm	17.2	28.6	28.9	22.8	24.37
Hf	ppm	4.7	2.7	3.3	3.2	3.47
Nb	ppm	11.8	4.9	6.4	8.4	7.87
Rb	ppm	109.5	47.6	62.9	83.6	75.90
Sn	ppm	3	3	1	3	2.50
Sr	ppm	240.2	631.1	551.6	342.3	441.30
Ta	ppm	0.8	0.3	0.4	0.6	0.52
Th	ppm	10	3.8	5.4	6.9	6.52
U	ppm	6.1	11.7	9.4	10.2	9.35
V	ppm	135	172	166	201	168.50
W	ppm	3.4	10.3	8.6	6	7.07
Mo	ppm	87.1	326.5	142.1	71.4	156.77
Cu	ppm	30.1	43.2	35.6	27.0	33.97
Pb	ppm	26.6	44.5	29.4	31.5	33
Zn	ppm	192	293	196	230	227.75
Ag	ppm	3.0	2.2	2.6	2.9	2.67
Li	ppm	234	177.3	188.1	201.4	200.20
Zr	ppm	184.7	109.5	137.9	137.2	142.32
Mn/Fe	–	0.49	1.36	0.92	0.21	0.74
Growth rate	mm/yr^{-1}	0.134	0.006	0.008	0.049	0.049

REE CONTENT

The REE content in Baltic nodules studied during our research (App. 2) is lower than in the deep-marine Fe-Mn nodules (Ingri, Ponter, 1987), but is similar to the amount of REE in nodules from other parts of the Batlic Sea (Ehrlich, 1968). The REY content is comparable to PAAS (Fig. 8; McLennan, 1989). The total average amount of REE + Y in analyzed samples is 165.11 ppm, ΣLREE 145.72 ppm, and ΣHREE 19.39 ppm. It is visible that the LREE content is enriched in comparison to HREE. A negative cerium anomaly was identified in the samples, which is characteristic for diagenetic nodules (Hein, Koschinsky, 2014). The maximum HREE/LREE ratio is 8.1. The samples show a small positive europium anomaly. The La and Ce contents in studied Baltic nodules (average 38.90 and 60.20 ppm, respectively) is lower than average results (52.6, 102.3 ppm, respectively) obtained by Baturin (2009) for nodules from the Gulf of Finland.

The current knowledge on distribution of REE in minerals of Baltic nodules is insufficient (Szefer *et al.*, 1999). Pattan *et al.* (2008) considered that the presence of REE is strictly dependent of the presence of the authigenic phase Fe + Ti + P. On the other hand, Nath *et al.* (1992) suggested

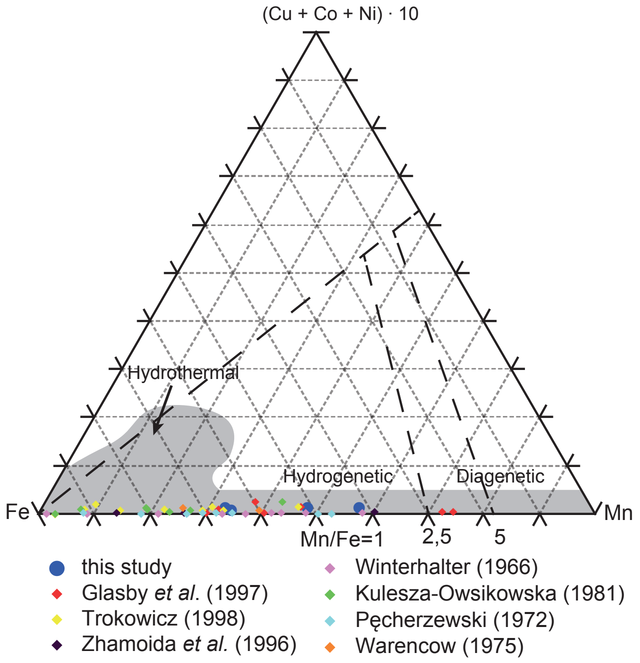

Fig. 6. Ternary diagram for ferromanganese genetic models (after Bonatti *et al.*, 1972)

Trójkątny diagram klasyfikacyjny dla określenia genezy konkrecji (Bonatti i in., 1972)

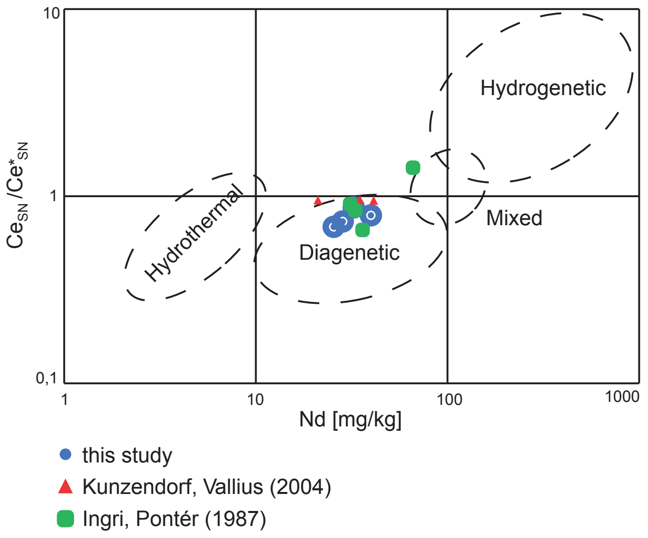

Fig. 7. Diagram for determination of origin of Fe-Mn nodules (after Bau *et al.*, 2014)

Diagram klasyfikacyjny genezy konkrecji (Bau i in., 2014)

that REE are attributed to separated Fe and P phases. Some researchers (Dubinin *et al.*, 2008; Duliu *et al.*, 2009; Prakash *et al.*, 2012) considered that the REE presence is associated with both hydrogenetic Fe oxide-hydroxides and diagenetic hydroxyapatite enriched in Fe by diadochy. LREE are usually linked with Mn oxide phases, while HREE with Fe oxide-hydroxides. The correlation of REE with Fe + P + Ti shows low correlation r = 0.31. Similar data are associated with the separated phases of Fe (r = 0.32) and Mn (r = 0.33). No correlation of REE with phosphorous is visible due to the lack of dispersed fine phosphate phases. The increasing REE content is related to the decreasing Mn/Fe ratio. The indicated dependencies were calculated by only a few analyses and it is necessary to confirm/refuse them in future examinations based on a greater population of nodule samples and analytical data.

The short drill cores from Baltic sediments are characterized by slight enrichment of LREE. The La content decreases towards the surface, which suggests that REE may be leached after deposition and then be transported in solution (Kunzendorf, Vallius, 2004). The process of dissolution of Baltic nodules was widely discussed by Vasiljeff (2015).

CONCLUSIONS

Fe-Mn Baltic nodules collected from the sea bottom of the Polish Maritime Areas indicate a wide range of sizes and morphologies. There are three main types of nodules: discoidal D, irregular I, and transitional D-I. All of the types contain three groups of mineral constituents: 1) red Fe oxyhydroxides, 2) black Mn oxyhydroxides, and 3) a group of terrigenous minerals represented by quartz, plagioclase, K-feldspar, glauconite and a small amount grains of heavy minerals. The heavy fraction is composed of ilmenite, rutile, authigenic monazite and barite.

Based on the Fe, Mn and (Cu + Co + Ni) content, the origin of studied nodules is determined as hydrogenetic, while using REE (Ce$_{sn}$/Ce$_{sn}$ · vs. Nd) – as diagenetic. Further stages of detailed examinations, especially of Mn-minerals, should provide the unequivocal conclusion on the origin, but currently it is already possible to conclude that the nodules are

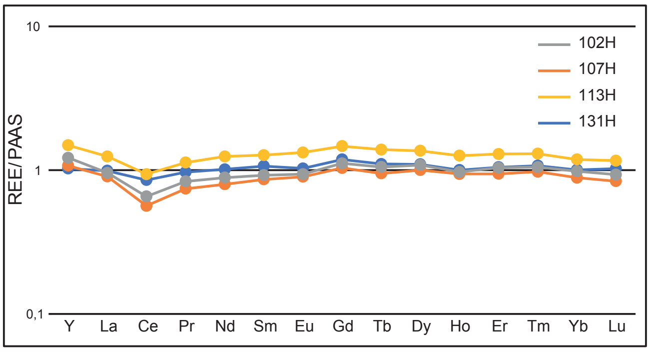

Fig. 8. PASS-normalized distribution of rare earth elements in nodules

Rozkład zawartości REE normalizowany do PASS at the early stage of diagenetic processes, or even that their origin is diagenetic.

The study of their chemical composition shows diverse values of metals and REE. The highest concentrations of metals are found for Li, Ba and Sr. These metals are related to plagioclase and Ba sulphate. The amounts of Zn, Co, Cu and Ni are sub-economic. The total amount of REE is at a medium level (in comparison to PASS) and varies from 134.22 to 204.04 ppm. The samples are characterized by a negative cerium anomaly and a slightly positive europium anomaly.

The growth rate of Fe-Mn nodules has been estimated using a cobalt chronometer, and ranges from 0.006 to 0.134 mm/yr^{-1}.

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PODSUMOWANIE

Bałtyckie konkrecje Fe-Mn wydobyte z powierzchni dna polskich obszarów morskich są zróżnicowane pod względem wielkości i morfologii. Występują 3 główne rodzaje konkrecji: dyskoidalne D, nieregularne I i przejściowe D-I. Konkrecje zawierają 3 grupy składników: 1) czerwone tleno-wodorotlenki Fe, 2) czarne tleno-wodorotlenki Mn, 3) oraz grupę minerałów terygenicznych reprezentowanych przez kwarc, plagioklazy, skalenie potasowe, glaukonit i niewielką ilość minerałów ciężkich. Frakcja ciężka składa się z ilmenitu, rutylu, autigenicznego monacytu oraz barytu. Na podstawie zawartości Fe, Mn i Cu + Co + Ni ustalono, że konkrecje są genezy hydrogenicznej, używając zależności REE (Ce_{sn}/Ce_{sn} · vs. Nd) jako diagenetyczne. Następne etapy szczegółowych badań, głównie minerałów Mn, mogą pozwolić na jednoznaczne określenie pochodzenia konkrecji, ale już teraz można wnioskować, że znajdują się one we wczesnym stadium procesów diagenetycznych lub są pochodzenia diagenetycznego. Konkrecje wykazują zróżnicowaną zawartość metali oraz pierwiastków ziem rzadkich. Najwyższe koncentracje metali dotyczą: Li, Ba i Sr. Metale są związane z plagioklazami oraz minerałami Ba, Zn, Co, Cu i Ni. Taka ilość metali nie ma znaczenia gospodarczego. Całkowita zawartość REE jest na średnim poziomie (w porównaniu do PASS) i zmienia się od 134,22 do 204,04 ppm. Próbki charakteryzują się negatywną anomalią cerową oraz niewielką pozytywną anomalią europową. Tempo wzrostu konkrecji Fe-Mn określono z użyciem chronometru kobaltowego. Wartość tempa wzrostu w badanych konkrecjach wynosi od 0,006 do 0,134 mm/yr^{-1}.