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# Rare earth elements pilot studies of the baltic marine sands enriched in heavy minerals

## Introduction

The use of a number of elements that rarely formed economic deposits, but they are of major importance for the economy of the countries in the European Union is of key importance in modern industrial production. The rare earth elements (REE), which were considered critical for the economic development of the most developed countries of the EU are among these elements (Opinion 2006; Galos and Smakowski 2008; EU Resolution 2011; Moss et al. 2011; Smakowski 2011; Szamałek 2011; Galos et al. 2012). The most important among the latest REE technologies are: lanthanum, europium, erbium and neodymium (Chakhmouradian and Wall 2012; Haque et al. 2014; Paulo and Krzak 2015).

In recent years, the global production of rare earths oxides (REO) has been at the level of the 123–124 thousand tons/year (Smakowski et al. 2012; USGS minerals, 2016). The rare earth metals market is controlled by China, which has the world's largest resources (> 20%; approx. 55 million tons) and annually provides more than 95 percent of the demand for rare earth materials (Hatch 2012). Chinese restrictions in the export of REE over the past few years have led to international concerns about future supply shortages

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(Klupa 2012). Despite this fact, the world REE resources are giant (about 130 million tons REO; USGS minerals, 2016) and sufficient to cover the current volume of demand for more than 1,000 years.

Minerals that contain REE occur in the form of primary and secondary concentrations in several genetic types of deposits (Paulo 1999). The most important among the primary deposits are those related to alkaline magmatic complexes and carbonatites (Mariano and Mariano 2012; Kynicky et al. 2012). The main ore minerals in these deposits are: bastnäsite [La,Ce,Y $(CO_3)$F], allanite [$(Ce,Ca,Y)_2(Al,Fe{+}{+}{+})_3$ $(SiO_4)_3(OH)$], monazite [(Ce,La,Nd,Th) $PO_4$, apatite [$Ca_5(PO_4)_3(OH,F,Cl)$] and pyrochlore [$(Na,Ca)_2Nb_2O_6(OH,F)$]. The placer deposits, especially sands from the shoreline formation (Ti-Zr-REE-Th), in which the REE-bearing minerals are primarily, monazite, and xenotime [YPO4] that occur with zircon [Zr $(SiO_4)$], ilmenite [$FeTiO_3$] and from the second formation represented by cassiterite sands [$SnO_2$] (Sn-Ta-Nb-Y) with xenotime (Long et al. 2010; Szamałek et al. 2013) are also important. In the first formation, the content of REE-bearing minerals (mainly monazite) ranges from 0.3 to 5% among heavy minerals (in India to 20%; Paulo and Krzak 2015). In turn, the share of heavy fraction can be from 3 to 60% of quartz sands that form the mainly coastal bars. Monazite and xenotime are by-products of the enrichment of ilmenite-zircons sands. The production of this type heavy minerals concentrates is carried out mainly in Western Australia, Brazil and India (Collins and Baxter 1984; Hedrick 1997; Long et al. 2010; Paulo and Krzak 2015). In turn, the production of cassiterite concentrates (along with xenotime) on the largest scales takes place on the shelf in the south-eastern Asia (e.g. in Malaysia, Thailand and Indonesia; Economic 1988; Hedrick 1997; Szamałek et al. 2013).

In Poland, the perspective of REE deposit occurrence, despite the evidence of their resources in the two deposits in the Sudety Mountains (Kanasiewicz 1987), were judged very critically by some researchers (Paulo 1993). Recognized in NE Poland by deep drilling REE mineralization associated with carbonatites and alkaline magmatism is not of any economic importance to date (Kubicki 1987; Krzemińska and Krzemiński 2012, and references therein). Marine sands from the Polish coast and bottom of the Baltic Sea were also the subjects of works in the field of the concentration of REE in heavy minerals. These studies focused around three main issues: the composition of heavy minerals and conditions of placers formation (Zwierzycki 1947; Sawicka 1953; Łoziński and Masicka 1959; Mączka and Racinowski 1960; Wajda 1970, 1977; Kotliński 1985; Kramarska 1991) prognoses of resources (Kotliński and Kramarska 1977; Jurowska et al. 1978; Wajda 1980, 1982; Mapa geologiczna… 1989–1995; Kramarska 1993; Jones 1994; Kramarska et al. 2005) and the implementation issues relating to the technology of extraction, processing and the use of components especially in marine sands from the Odra Bank, Słupsk Bank and from the Łeba region (Akerman and Krajewski 1959; Juskowiak et al. 1976; Rosińska 1981; Łuszczkiewicz 1984; Łuszczkiewicz et al. 1988; Bagdach and Lasko 1989). Oder Geological documentation of heavy minerals and sands resources in D categories were made for the Odra Bank (ca. 13 323.20 thousand tons, including 505.74 thousand tons of heavy minerals; Kaulbarsz et al. 2013).

In this article we present the pilot REE results in several samples of marine sands collected from the Polish coast of the Baltic Sea and sandbanks of the southern Baltic that were made in PIG-PIB under the theme of Mikulski et al. (2014). Other data in terms of REE distribution in other geological areas in Poland are presented in separate articles (Mikulski et al. 2015; Brański and Mikulski 2016; Oszczepalski et al. 2016).

## 1. Distribution and genesis of heavy minerals concentration in the Baltic marine sediments

The Pleistocene deposits of glacial and fluvioglacial accumulation that were subject to different in time processes of abrasion and re-deposition are the direct source of heavy minerals in marine sediments in the Baltic Sea (Sawicka 1953; Łoziński and Masicka 1959; Kotliński 1985). Concentrations of certain minerals in the marine sands are of secondary nature. The source rocks for these minerals are crystalline and sedimentary rocks of Scandinavia and the bottom of the Baltic Sea. The accumulation of heavy minerals is associated with the selective implementation of the movement of mineral grains of a defined size and habit, under the influence of bottom currents and a complex mechanism of grain transportation (Leontjew et al. 1982; Haas et al. 1995; Dill 2007; Dill et al. 2012). Heavy minerals from the Baltic sands are represented by transparent components (quartz, garnet, amphibole, pyroxene, epidote, chlorite, and biotite) and opaque minerals (mainly ilmenite, and rarer by magnetite). Participation of other minerals (glauconite, staurolite, tourmaline, zircon, rutile, andalusite, sillimanite and apatite) and other mineral groups (e.g. carbonates) is subordinate (Sawicka 1953; Wajda 1970; Jurowska et al. 1978). The contents of heavy minerals (tested mainly in the 0.25–0.125 mm fraction) is mostly from 1 to 2%. Concentrations above 3 weight % create an isolated field in the sands, in the shallow water of the sea within the range of the intense impact of wave and bottom currents, typically to a depth of the sea 10–30 m, and a little deeper on the thresholds separating deep-water basins (Mapa… 1989–1995; Kramarska et al. 2005).

The analysis of the distribution of concentration and granular grain composition of sediments indicates that perspective, in terms of exploration, are sediments associated with the relics of the bay-bar accumulation from the period of the Littorina Baltic Sea transgression in the Middle Holocene (Jurowska et al. 1978; Kramarska 1998). High concentrations of up to 20% occur in the sands of Odra Bank, a designated string shoals from the Eastern arm of this form to Kołobrzeg (Kramarska et al. 2005). Less well preserved relics of the spit, with the extremely high concentration of heavy minerals in the Polish zone of the Baltic Sea up to 45%, occur in Central and Eastern parts of the Słupsk Bank (Kotliński and Kramarska 1977).

On the Słupsk Bank, the total area of the three fields with the concentration of heavy minerals is a dozen km$^2$. The contents of fractions 0.063–0.25 mm in length is more than

90%. Enrichment of heavy minerals in the laminas (2–10 mm thick) are correlated with the subsurface layer of the sands at about 30 cm of the thickness (Kotliński and Kramarska 1977).

On the Odra Bank, the documentation of resources only covers two placer fields (box A and box B, a total of approximately 1,303.49 ha) in the prospective areas (Kramarska et al. 2016). The contents of heavy minerals ranges from 1.7–21.7 weight %. Placer concentrations reflect the high degree of mineralogical selection of mature granulometric deposits of shoals. Enriched sands from the Odra Bank contain, as a rule, more than 80% of the very fine and fine-grained fraction (0.063–0.25 mm) and are well or very well sorted. A layer enriched with heavy minerals, consists of lamina and streaks, a less laminae thickness of several cm, alternately enriched and poor in heavy minerals. The highest enrichment in heavy minerals is present on the bottom surface and gradually decreases with depth. The enriched layer maximum may reach up to 1 m. The average share of heavy minerals in a layer thickness of 0.5 m occurring directly from the bottom surface is about 4.5% and decreases to 2.5–4% at a depth of 0.5–1 m.

Heavy mineral resources in the sands of A and B fields have been estimated at about 505 thousand tons, including about 25 thousand tons of zirconium, almost 200 thousand tons of titanium minerals (ilmenite, rutile and leucoxene) and about 160 thousand tons of garnets (Kaulbarsz et al. 2013; Kramarska et al. 2016).

## 2. The methodology and scope of research

In this paper, rare earth elements were examined in 7 samples of marine sands, collected from the cores of archive boreholes drilled in the region of the Odra Bank, Słupsk Bank and in two samples from the Hel Peninsula (Fig. 1). Three tagged samples: V201, V210 and V225 come from the subsurface sections of the cores (0–0.5 m) with the same names, and represent the natural sands with heavy minerals (Fig. 2). Cores were collected with use of a vibro-corer during geological documentation works (Kaulbarsz et al. 2013).

Samples of ŁO(Zr) and ŁS(Zr) come from zirconium concentrates obtained in the processes of enrichment, separation and recovery of heavy minerals from marine sands (Bagdach and Lasko, 1989). The ŁO(Zr) sample constitutes the zirconium concentrate recovered from the sands of the Odra Bank, where sand weighing 1.2 thousand tons contained an average of 1.72% heavy minerals. While ŁS (Zr) zirconium concentrate sample was made from sands of the Słupsk Bank and primary sand sample weighing 2 thousand tons contained an average of 4.2% of heavy minerals (ibid.).

The samples with the symbols He1 and He2 were collected on the Hel Peninsula from a 16.6 km stretch of beach. A sample of the sands (He1; 10/13/13) was taken from the beach drift (Fig. 2a), and sample (He2; 10/13/14) from the same place but from the score in the trench with a depth of 1 m (Fig. 2b). The 2 samples mentioned above were the subject of classic panning and heavy mineral concentrates were obtained. The He1 sample of marine

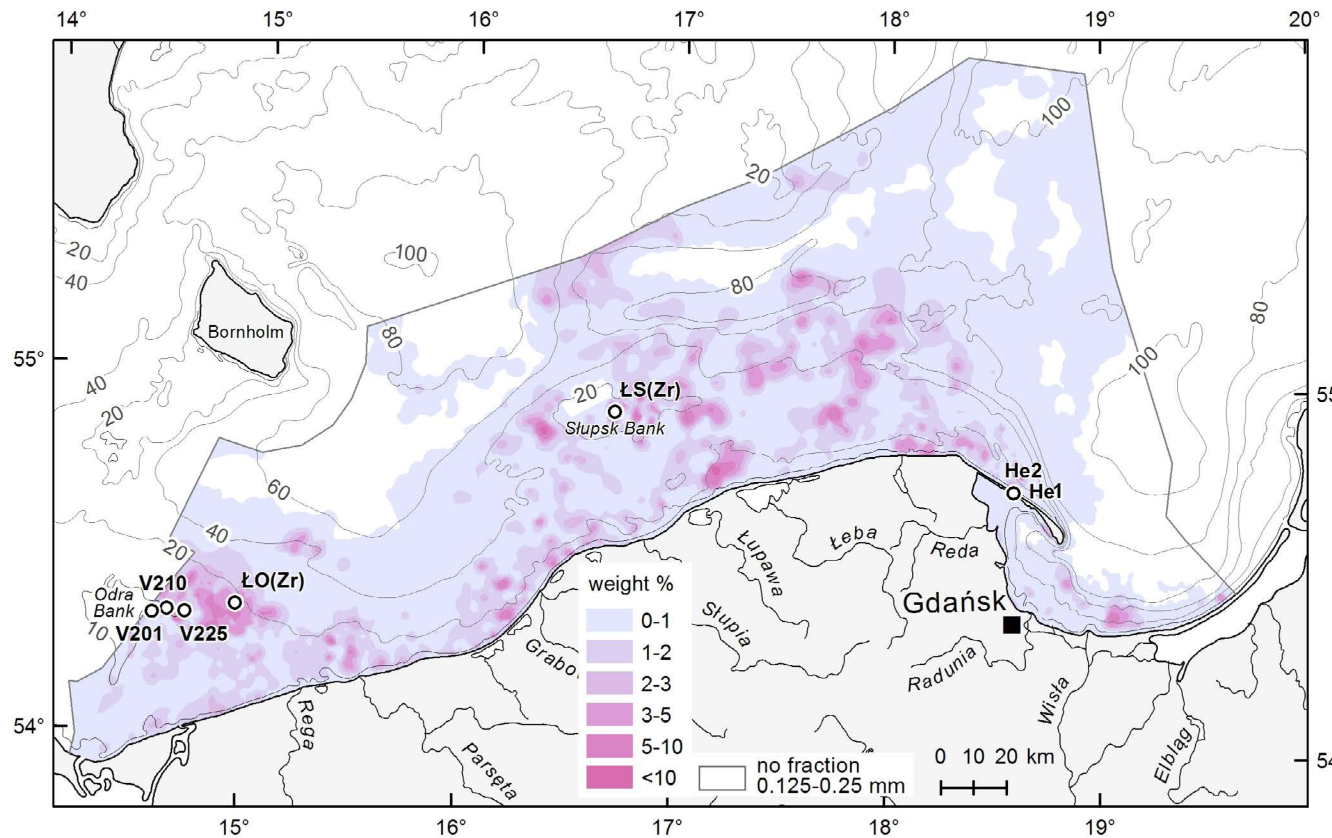


Fig. 1. The location of the samples site collected for REE analyses on the background of the map contents of heavy minerals in the surface bed of sands (fraction 0.125–0.25 mm) in the Polish marine territory (after Kramarska et al. 2005)

Rys. 1. Lokalizacja próbek pobranych do analiz REE na tle mapy zawartości minerałów ciężkich w powierzchniowej warstwie piasków (frakcja 0,125–0,25 mm) w polskich obszarach morskich (wg Kramarska i in. 2005)


Fig. 2. Marine sands samples enriched in heavy minerals
a) V201 borehole, depth 0–0.5 m, b) V210 borehole, depth 0–0.5 m. Odra Bank

Rys. 2. Próbki piasków morskich wzbogacone w minerały ciężkie
a) Wiercenie V201, głęb. 0–0,5 m, b) Wiercenie V210, głęb. 0–0,5 m. Ławica Odrzana

sands contained about 30.9 % heavy minerals and He2 sample has only about 0.14 % heavy minerals. All the sand samples were subject of REE analyses.

Rare earth elements, Sc, Y, and Th analyses were performed at the Chemical Laboratory of the Polish Geological Institute – National Research Institute, using mass spectrometry with inductively coupled plasma mass spectrometry (ICP-MS technic). After acid digestion, the samples were diluted 20 times with a solution of 1% $HNO_3$. The total solution of

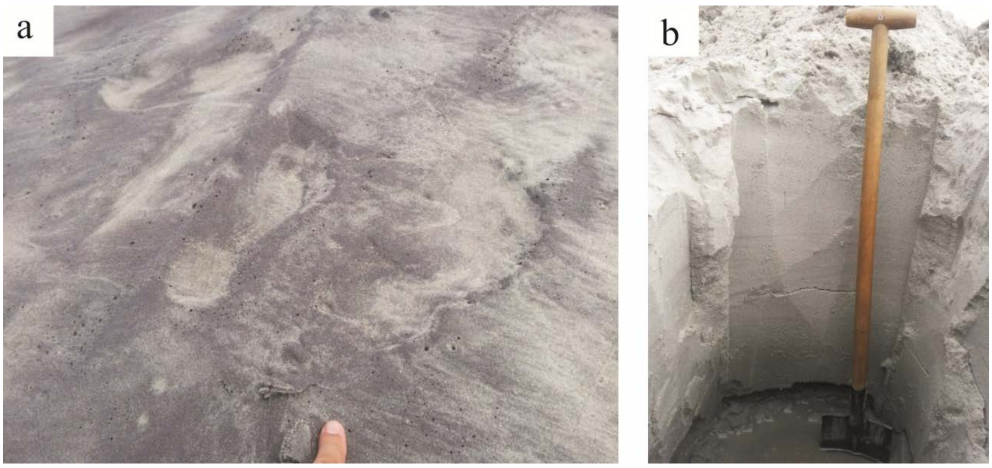


Fig. 3. a) Beach sands from the upper near shore zone enriched in heavy minerals (He1),
b) Trench in order to collect the profile sample with a width of 5 cm and a height of ca. 1 m (He2)

Rys. 3. a) Piaski plażowe ze strefy przyboju silnie wzbogacone w minerały ciężkie (próbka He1),
b) Wkop w celu pobrania próbki bruzdowej o szerokości 5 cm i wysokości około 1 m (próbka He2)

elements contained in the samples was achieved by the use of hydrofluoric acid and chloric acid (VII – oxidation of fluorine and chlorine in acid). Dried and powdered samples were initially treated with nitric acid (V) in order to distribute organic matter and dissolved in a mixture of perchloric and hydrofluoric acid (VII). In order to improve the procedure for dissolution, digestion was repeated three times. In the last stage, after evaporation to dryness (on a hot plate, to a temperature of 150°C ± 10°C) the residue was dissolved in dilute nitric acid (V). The solution obtained was submitted for analysis by ICP-MS. Detection limits were 0.5 ppm for LREE and 0.05 ppm for HREE.

The concentrates were made from heavy minerals samples and sections were polished for the work under the polarizing microscope (NIKON ECLIPSE LV100 POL) and electron microprobe (CAMECA SX-100). Specifications were as follows: voltage – 15 kV, current beam 10, beam focused. Acquisition times: in the peak position-20 s, the position of the background-10 s. Depositing carbon. The following spectral lines were examined: Ce – Lα, La – Lα, Pr – Lβ, Nd – Lβ, Sm – Lβ, Gd – Lβ and Dy – Lα. The lines were selected in order to avoid interference. Analyzed on the crystals type LLIF. Standards: – synthetic glass doped with REE made by P&H Company.

## 3. Results of the rare earths studies in the marine sands of the Baltic Sea enriched in heavy minerals

### 3.1. Odra Bank

The following V201, V210 and V225 core samples represent fine-grained sands with the dominance of 0.125–0.25 mm fraction (usually > 70%). The main admixture constitutes the 0.25–0.5 mm fraction, which occurs in quantities from several dozen to about 30% (Kaulbarsz et al. 2013). The heavy minerals content in samples being the subject of REE analyses belongs to the highest in the entire area of the Odra Bank covered by the resource evaluation. In the trench (profile) samples (V225 and V210) collected from the upper (0–0.5 m) part of the cores, their content are 4.64 and 6.15%, respectively. The highest contents of heavy minerals (c.a. 21.7% weight %) was found in the V201 sample. In a layer from a depth of 0.5–1 m below the seabed the heavy minerals contents falls below 3 weight %. Research of the 20-centimeter core segments shows a progressive decline in heavy minerals content with the depth.

Rare earth elements and thorium were found as a result of the carried out ICP-MS chemical analysis in the all samples (Table 1). Mainly a group of the light lanthanides with a high content of cerium, lanthanum and neodymium occurs in the marine sand samples. The content of yttrium, which in the V201 sample is dominant over the rare earths, is noteworthy. The thorium content is much lower than the listed elements. There is a clear relationship

Table 1. The content of REE, Sc, Y, and Th in marine sands as well as in the heavy minerals concentrates [samples: ŁO(Zr) and ŁS(Zr)] from the southern Baltic bottom and of the Hel Peninsula beach

Tabela 1. Zawartości REE, Sc, Y i Th w próbkach piasków morskich jak również w koncentracie minerałów ciężkich [próbki: ŁO(Zr) and ŁS(Zr)] z dna południowego Bałtyku i plaży Półwyspu Helskiego

| Sample | ∑REE | Sc | Y | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | Th |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| number | mg/kg | | | | | | | | | | | | | | | | | |
| V201 | 156.15 | 23.2 | 69.0 | 24.5 | 51.7 | 6.2 | 24.3 | 5.27 | 0.74 | 5.81 | 1.28 | 10.28 | 2.59 | 9.08 | 1.54 | 11.1 | 1.76 | 11.32 |
| V210 | 92.93 | 7.9 | 25.6 | 16.8 | 35.4 | 4.2 | 16.0 | 3.20 | 0.42 | 3.03 | 0.57 | 4.09 | 0.97 | 3.21 | 0.54 | 3.88 | 0.62 | 7.58 |
| V225 | 63.03 | 2.5 | 9.7 | 12.9 | 26.3 | 3.0 | 11.3 | 2.14 | 0.26 | 1.74 | 0.28 | 1.72 | 0.37 | 1.20 | 0.19 | 1.41 | 0.22 | 6.09 |
| ŁO(Zr) | 8 786.7 | 14.7 | 332.0 | 1 947.1 | 3 921.7 | 465.9 | 1 735.0 | 297.09 | 10.86 | 208.52 | 23.33 | 99.10 | 14.21 | 33.5 | 4.07 | 22.8 | 3.55 | 892.16 |
| ŁS(Zr) | 5 117.54 | 15.9 | 276.4 | 1 153.8 | 2 324.5 | 267.0 | 960.5 | 154.43 | 6.45 | 107.22 | 13.22 | 67.72 | 10.22 | 26.7 | 3.67 | 23.3 | 3.79 | 473.82 |
| He1 | 41.74 | 1.2 | 5.5 | 8.4 | 17.8 | 2 | 7.8 | 1.48 | 0.24 | 1.22 | 0.18 | 1.02 | 0.21 | 0.6 | 0.1 | 0.61 | 0.1 | 3.13 |
| He2 | 1 371.16 | 38 | 134 | 290 | 600 | 68.4 | 256 | 46.7 | 1.62 | 34.9 | 4.76 | 26.2 | 5.07 | 15.6 | 2.4 | 17 | 2.6 | 147 |

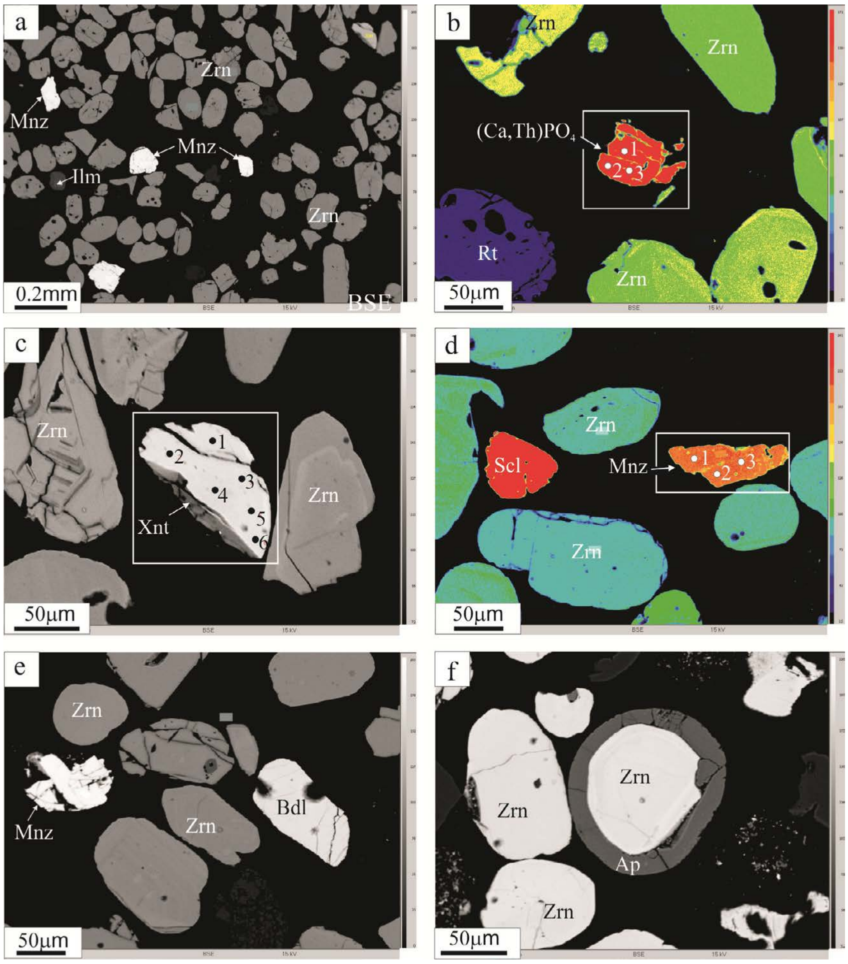


Fig. 4. The heavy minerals concentrate from the Odra Bank with visible well-rounded grains. Sample no. LO/P-4 a) Zircon grains dominate among minerals in the concentrate (Zrn; darkgrey). Monazite grains (Mnz; white) are subordinate and ilmenite (Ilm) appears as single grains. Back-Scattered Electron Image (BSEI) /field 01/photo-1 see Table 2, b) BSEI in artificial colors reveals different minerals in heavy minerals concentrate; (Ca,Th)PO4 – Th apatite; Rt – rutile; Zrn – zircon, c) Grains of zircon (Zrn) and xenotime (Xnt) with visible point of SEM analyses. BSEI/field 04/photo-2, d) BSEI in artificial colors reveals different minerals in heavy minerals concentrate; Scl – scheelite; Zrn – zircon; Mnz – monazite. BSEI/field 02/photo-2, e) Well-rounded zircon grains (Zrn) together with baddeleyite (Bdl) and monazite (Mnz). BSEI. Grain of zircon (Zrn) with apatite (Ap) rim. BSEI

Rys. 4. Koncentrat minerałów ciężkich z Ławicy Odrzanej z widocznym dobrym obtoczeniem ziarn. Próbka nr LO/P-4 a) Ziarna cyrkonu dominują ilościowo w koncentracie minerałów ciężkich (Zrn; ciemnoszary). Ziarna monacytu (Mnz; biały) są ilościowo podrzędne i podobnie jak ilmenit (Ilm) występują jako pojedyncze ziarna. Obraz elektronów wstecznie odbitych (BSEI) /obszar 01/foto-1 patrz tab. 2, b) Obraz elektronów wstecznie odbitych w sztucznych barwach uwypukla różnice w obecności minerałów w koncentracie; (Ca,Th) PO4 – Th apatyt; Rt – rutyl; Zrn – cyrkon, c) Ziarna cyrkonu (Zrn) i ksenotymu (Xnt) z widocznymi punktami analiz SEM. BSEI/obszar 04/foto-2, d) BSEI w sztucznych barwach uwypukla różnice w obecności minerałów w koncentracie; Scl – scheelite; Zrn – cyrkon; Mnz – monacyt. BSEI/obszar 02/foto-2, e) Dobrze obtoczone ziarna cyrkonu (Zrn) w towarzystwie z baddeleyitem (Bdl) i monacytem (Mnz). BSEI. Ziarno cyrkonu (Zrn) z otoczką apatytu (Ap). BSEI of the REE content with the presence of heavy minerals in sediments. The highest concentrations of rare earth elements are present in the V201 sample, which has c.a. 21.7 weight % of heavy minerals. They are most often 2–3 times higher than in V210 and V225 samples.

Zircon dominates in the heavy minerals concentrate (ŁO(Zr) and the contents of rare earth elements is many times higher (even 100 times) than in the natural marine sands. The light lanthanides also dominate in the zircon concentrate sample ŁO(Zr). The cerium concentration reaches 3.9 g/kg, and lanthanum and neodymium occur in the amount of 1.9 and 1.7 g/kg. The contents of praseodymium, yttrium, gadolinium and samarium are in the range of 0.5–0.2 g/kg. Components of the subgroups of heavy lanthanides are in the range from several to almost 100 mg/kg. In relation to the contents of the lanthanides in comparison to their content in sand samples, the content of yttrium is low (332 mg/kg) and scandium (14.7 mg/kg) was negligible. However, thorium reaches almost 0.9 g/kg of concentrate. Microscopic and microprobe research revealed a concentrate of the dominant presence of zircon in the ŁO(Zr) sample and also the appearance other heavy minerals such as garnet, topaz, rutile or apatite (in total of up to a dozen percent volume of concentrate). Zircons are well rounded and generally have sizes c.a. of 100 μm in length (range from 80 to 150 μm). They show different content for Hf and a varied admixture of yttrium. monazites which are the main media of LREEO (55–60 weight %) and Th (c.a. 3–8 weight %; Table 2) have up to several percent in concentrate. Monazites, like zircons are well rounded and the sizes of the grains are in the range from 100 to 250 μm (Fig. 4a, 4d–e). Xenotime single well-rounded grains are up to 100 μm in diameter (Fig. 4c) and apatite grains were also found (Fig. 4b). Apatite grains are slightly smaller in size (50–70 μm in diameter) and may form very spectacular rims around the zircon core (Fig. 4f). It's a variety rich in thorium occurs among apatite (up to 47.6 weight % Th; Table 3). Xenotime has a high yttrium contents (43–44 weight % of $Y_2O_3$) and an admixture of HREEO (sum >15 weight %; Table 3). Rutile (without Nb-additives), and ilmenite also occur in heavy concentrations, however in subordinate quantities. Single grains of baddeleyite or scheelite (with a diameter of approx. 70 μm) were also found (Fig. 4d–e).

### 3.2. Słupsk Bank

The light lanthanides also dominate in the heavy minerals concentrate of the ŁS(Zr) sample from the Słupsk Bank. The cerium concentration reaches 2.3 g/kg, and lanthanum and neodymium is present in the amount of 1.1 and 0.96 g/kg, respectively (Table 1). Praseodymium, yttrium, gadolinium and samarium occur in contents from 0.1 to 0.3 g/kg. Components of the subgroups of heavy lanthanides are in the range of several (Lu, Tm) to almost 68 mg/kg (Dy). Compared with the sand samples, there is a low content of yttrium (276 mg/kg) and negligible of scandium (15.9 mg/kg) in relation to the other lanthanides. However, thorium reaches nearly 0.5 g/kg in the concentrate.

Table 2. WDS composition (in wt.%) of monazite grains in the heavy minerals concentrate from the Odra Bank (LO-P-4)

Tabela 2. Skład chemiczny (w % wag.) monacytu z koncentratu minerałów ciężkich z Ławicy Odrzanej (LO-P-4) na podstawie badań na mikrosondzie elektronowej (EPMA)

| | LO_P-4_area-02_phot-2 | | | LO_P-4_area-03_phot-2 | | | | LO_P-4_area-03_phot-3 | | | LO_P-4_areaz-07_phot-1 | | | LO_P-4_area-08_phot-1 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Formula | 1 / 1 | 2 / 1 | 3 / 1 | 1 / 1 | 2 / 1 | 3 / 1 | 4 / 1 | 1 / 1 | 2 / 1 | 3 / 1 | 1 / 1 | 2 / 1 | 3 / 1 | 1 / 1 | 2 / 1 | 3 / 1 |
| Weight % Oxide | | | | | | | | | | | | | | | | |
| S | 0.004 | 0.004 | 0.011 | 0.016 | 0.013 | 0.006 | 0.007 | 0.008 | 0.023 | 0 | 0.008 | 0.012 | 0.012 | 0.008 | 0.008 | 0.006 |
| $K_2O$ | 0.003 | 0 | 0.011 | 0.002 | 0.005 | 0.021 | 0.003 | 0.015 | 0.011 | 0.012 | 0.019 | 0.003 | 0.001 | 0.003 | 0 | 0.006 |
| CaO | 1.184 | 1.165 | 1.228 | 1.086 | 1.154 | 1.143 | 1.136 | 1.834 | 1.828 | 1.784 | 0.549 | 0.527 | 0.516 | 0.977 | 1.019 | 0.992 |
| FeO | 0.026 | 0.003 | 0.024 | 0 | 0.009 | 0.012 | 0.004 | 0.026 | 0 | 0.022 | 0 | 0 | 0 | 0.005 | 0 | 0.044 |
| SrO | 0.031 | 0.015 | 0 | 0.023 | 0.028 | 0.01 | 0 | 0.001 | 0 | 0.004 | 0.028 | 0.03 | 0.018 | 0 | 0.037 | 0.043 |
| PbO | 0.69 | 0.622 | 0.687 | 0.445 | 0.485 | 0.505 | 0.502 | 0.833 | 0.83 | 0.783 | 0.305 | 0.305 | 0.298 | 0.481 | 0.482 | 0.506 |
| $Al_2O_3$ | 0.006 | 0.012 | 0 | 0 | 0.025 | 0.019 | 0.031 | 0 | 0 | 0.014 | 0.026 | 0.024 | 0.028 | 0.024 | 0.002 | 0.007 |
| $Y_2O_3$ | 1.217 | 1.334 | 1.274 | 1.211 | 1.36 | 1.287 | 1.13 | 3.494 | 3.358 | 2.252 | 1.01 | 0.919 | 0.947 | 0.393 | 0.475 | 0.415 |
| $La_2O_3$ | 13.369 | 13.279 | 13.015 | 14.334 | 13.921 | 14.377 | 14.584 | 10.526 | 10.727 | 11.332 | 15.152 | 15.274 | 15.07 | 14.939 | 14.249 | 15.223 |
| $Ce_2O_3$ | 27.795 | 27.59 | 28.586 | 28.898 | 28.731 | 29.084 | 29.755 | 26.694 | 26.287 | 27.405 | 33.505 | 33.669 | 33.115 | 31.442 | 31.042 | 31.512 |
| $Pr_2O_3$ | 2.756 | 2.868 | 2.776 | 2.903 | 2.885 | 2.698 | 2.636 | 2.532 | 2.67 | 2.741 | 2.775 | 2.9 | 2.949 | 2.799 | 2.808 | 2.915 |
| $Nd_2O_3$ | 10.914 | 11.165 | 10.775 | 10.788 | 11.108 | 10.951 | 10.643 | 10.266 | 10.266 | 10.55 | 9.984 | 10.178 | 10.514 | 11.499 | 11.6 | 11.074 |
| $Sm_2O_3$ | 1.507 | 1.435 | 1.329 | 1.476 | 1.552 | 1.436 | 1.475 | 1.733 | 1.664 | 1.877 | 1.379 | 1.267 | 1.309 | 1.467 | 1.447 | 1.482 |
| $Eu_2O_3$ | 0 | 0.019 | 0.004 | 0 | 0 | 0 | 0 | 0 | 0 | 0.123 | 0 | 0 | 0 | 0 | 0 | 0 |
| $Gd_2O_3$ | 1.129 | 1.298 | 1.234 | 1.319 | 1.312 | 1.27 | 1.086 | 1.749 | 1.616 | 1.614 | 0.743 | 0.77 | 0.717 | 0.775 | 0.989 | 0.92 |
| $Dy_2O_3$ | 0.274 | 0.367 | 0.318 | 0.284 | 0.361 | 0.386 | 0.263 | 0.805 | 0.858 | 0.55 | 0.205 | 0.215 | 0.19 | 0.106 | 0.135 | 0.022 |
| $SiO_2$ | 1.109 | 1.078 | 1.185 | 0.529 | 0.516 | 0.497 | 0.471 | 0.392 | 0.417 | 0.475 | 0.55 | 0.547 | 0.574 | 0.521 | 0.574 | 0.565 |
| $ThO_2$ | 8.267 | 8.066 | 8.307 | 5.725 | 5.996 | 5.973 | 5.626 | 7.205 | 7.301 | 7.648 | 3.393 | 3.318 | 3.738 | 5.409 | 5.658 | 5.457 |
| $UO_2$ | 0.185 | 0.196 | 0.188 | 0.187 | 0.237 | 0.196 | 0.144 | 0.997 | 1.016 | 0.793 | 0.209 | 0.19 | 0.173 | 0.166 | 0.142 | 0.154 |
| $P_2O_5$ | 28.977 | 29.078 | 28.943 | 29.678 | 29.517 | 29.814 | 29.813 | 30.36 | 30.215 | 29.941 | 29.7 | 29.581 | 29.442 | 29.546 | 29.293 | 29.115 |
| $As_2O_5$ | 0 | 0 | 0 | 0 | 0 | 0 | 0.037 | 0.002 | 0.062 | 0.015 | 0 | 0.052 | 0 | 0 | 0 | 0 |
| Total | 99.443 | 99.594 | 99.893 | 98.904 | 99.215 | 99.683 | 99.342 | 99.472 | 99.146 | 99.935 | 99.539 | 99.783 | 99.61 | 100.558 | 99.961 | 100.458 |

Table 3. WDS compositions (in wt.%) of Th-apatite in the heavy minerals concentrate from the Odra Bank (LO-P-4-area-01-phot-1) and of xenotime grains from the Odra (LO-P-4) and Słupsk (LS-K-7) Banks

Tabela 3. Skład chemiczny (w % wag.) Th-apatytu z koncentratu minerałów ciężkich z Ławicy Odrzanej (LO-P-4-obszar-01-foto-1) oraz ksenotymu z Ławicy Odrzanej (LO-P-4) i Ławicy Słupskiej (LS-K-7) na podstawie badań na mikrosondzie elektronowej (EPMA)

| LO_P-4_area-01_phot-1 | | | | LO_P-4_area-04_phot-2 | | | | | | | | LS_K-7_area-06_phot-1 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Formula | 1/1 | 2/1 | 3/1 | Formula | 1/1 | 2/1 | 3/1 | 4/1 | 5/1 | 6/1 | 1/1 | 2/1 | 3/1 | 4/1 |
| Weight % Oxide | | | | | | | | | | | | | | |
| S | 0.025 | 0.066 | 0.01 | S | 0.008 | 0.008 | 0.014 | 0.01 | 0.008 | 0.007 | 0.023 | 0.024 | 0.028 | 0.017 |
| $K_2O$ | 0.253 | 0.168 | 0.208 | $K_2O$ | 0.003 | 0.019 | 0.012 | 0.011 | 0.014 | 0.014 | 0 | 0.005 | 0.011 | 0 |
| CaO | 11.06 | 10.206 | 9.623 | CaO | 0.2 | 0.208 | 0.216 | 0.174 | 0.241 | 0.115 | 0.147 | 0.05 | 0.1 | 0.194 |
| FeO | 0.167 | 0.173 | 0.221 | FeO | 0 | 0.04 | 0.025 | 0 | 0 | 0 | 0 | 0 | 0.021 | 0 |
| SrO | 1.695 | 1.616 | 1.508 | SrO | 0.01 | 0.006 | 0.059 | 0 | 0 | 0 | 0.01 | 0 | 0 | 0 |
| PbO | 0.039 | 0.064 | 0.066 | PbO | 0.31 | 0.274 | 0.326 | 0.283 | 0.438 | 0.132 | 0.059 | 0.005 | 0.054 | 0.076 |
| $Al_2O_3$ | 0.263 | 0.286 | 0.313 | $Y_2O_3$ | 43.565 | 43.734 | 44.065 | 44.752 | 43.71 | 43.619 | 38.962 | 40.525 | 39.91 | 38.512 |
| $Y_2O_3$ | 1.432 | 1.378 | 1.197 | $Nd_2O_3$ | 0.356 | 0.352 | 0.51 | 0.46 | 0.478 | 0.265 | 0.351 | 0.409 | 0.398 | 0.455 |
| $La_2O_3$ | 2.357 | 2.027 | 1.832 | $Sm_2O_3$ | 0.416 | 0.476 | 0.439 | 0.456 | 0.493 | 0.485 | 1.162 | 1.091 | 1.095 | 1.298 |
| $Ce_2O_3$ | 2.27 | 2.29 | 1.569 | $Eu_2O_3$ | 0 | 0.073 | 0.068 | 0.064 | 0.041 | 0.037 | 0.696 | 0.545 | 0.514 | 0.761 |
| $Pr_2O_3$ | 0.352 | 0.366 | 0.237 | $Gd_2O_3$ | 1.499 | 1.542 | 1.613 | 1.76 | 1.703 | 1.438 | 5.313 | 4.645 | 4.057 | 5.621 |
| $Nd_2O_3$ | 1.684 | 1.371 | 1.234 | $Tb_2O_3$ | 0.464 | 0.386 | 0.536 | 0.428 | 0.423 | 0.379 | 1.226 | 1 | 0.864 | 1.162 |
| $Sm_2O_3$ | 0.265 | 0.345 | 0.274 | $Dy_2O_3$ | 5.012 | 5.027 | 5.193 | 5.4 | 5.154 | 4.77 | 7.852 | 7.511 | 7.407 | 7.288 |
| $Eu_2O_3$ | 0.038 | 0.011 | 0.163 | $Ho_2O_3$ | 1.294 | 1.207 | 1.242 | 1.153 | 1.298 | 1.436 | 1.409 | 1.395 | 1.279 | 1.207 |
| $Gd_2O_3$ | 0.474 | 0.362 | 0.304 | $Er_2O_3$ | 4.195 | 4.199 | 3.932 | 4.054 | 3.915 | 4.661 | 3.214 | 3.286 | 3.699 | 2.941 |
| $Dy_2O_3$ | 0.21 | 0.246 | 0.217 | $Yb_2O_3$ | 4.648 | 4.569 | 3.955 | 3.875 | 4 | 6.192 | 3.48 | 3.879 | 4.625 | 3.696 |
| $SiO_2$ | 0.44 | 0.473 | 0.859 | $SiO_2$ | 0.258 | 0.282 | 0.316 | 0.223 | 0.384 | 0.157 | 1.4 | 1.882 | 2.335 | 0.809 |
| $ThO_2$ | 41.546 | 44.995 | 47.595 | $TiO_2$ | 0 | 0 | 0 | 0.039 | 0 | 0 | 0.335 | 0.376 | 0.477 | 1.076 |
| $UO_2$ | 0 | 0 | 0 | $ThO_2$ | 0.035 | 0.063 | 0.079 | 0.052 | 0.07 | 0.07 | 0.037 | 0 | 0.079 | 0.005 |
| $P_2O_5$ | 29.855 | 29.464 | 28.361 | $UO_2$ | 1.075 | 1.026 | 1.228 | 0.81 | 1.389 | 0.431 | 0.369 | 0.392 | 0.471 | 0.303 |
| $As_2O_5$ | 0 | 0.022 | 0.034 | $P_2O_5$ | 35.606 | 35.515 | 35.653 | 35.442 | 35.407 | 34.809 | 33.236 | 32.908 | 32.313 | 33.889 |
| Total | 94.426 | 95.929 | 95.824 | $As_2O_5$ | 0.035 | 0 | 0 | 0 | 0 | 0 | 0.147 | 0.086 | 0.055 | 0.063 |
| | | | | Total | 98.99 | 99.008 | 99.482 | 99.447 | 99.165 | 99.017 | 99.426 | 100.014 | 99.791 | 99.374 |

Table 4. WDS composition (in wt.%) of monazite grains in the heavy minerals concentrate from the Słupsk Bank (LS-K-7)

Tabela 4. Skład chemiczny (w % wag.) monacytu z koncentratu minerałów ciężkich z Ławicy Słupskiej (LS-K-7) na podstawie badań na mikrosondzie elektronowej (EPMA)

| | LS_K-7_area-04_phot-2 | | | | | LS_K-7_area-05_phot-1 | | LS_K-7_area-08_phot-1 | | LS_K-7_area-09_phot-1 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Formula | 1 / 1 | 2 / 1 | 3 / 1 | 4 / 1 | 5 / 1 | 1 / 1 | 2 / 1 | 1 / 1 | 2 / 1 | 1 / 1 | 2 / 1 | 3 / 1 |
| Weight % Oxide | | | | | | | | | | | | |
| S | 0.015 | 0.08 | 0.032 | 0.054 | 0.255 | 0.003 | 0.015 | 0.01 | 0.001 | 0.012 | 0.017 | 0.017 |
| $K_2O$ | 0.003 | 0.01 | 0.001 | 0.024 | 0.003 | 0.008 | 0.006 | 0.035 | 0.045 | 0.027 | 0.005 | 0.01 |
| CaO | 1.324 | 1.26 | 1.252 | 1.461 | 4.288 | 0.384 | 0.355 | 0.855 | 1.382 | 1.025 | 1.089 | 1.063 |
| FeO | 0.083 | 0.084 | 0.1 | 0.533 | 1.328 | 0 | 0 | 0.024 | 0.032 | 0.025 | 0 | 0 |
| SrO | 0.037 | 0.008 | 0.015 | 0.041 | 0.113 | 0.028 | 0.037 | 0.079 | 0.016 | 0.014 | 0.008 | 0.049 |
| PbO | 0.755 | 0.586 | 0.46 | 1.235 | 0.071 | 0.344 | 0.359 | 0.037 | 0.106 | 0.523 | 0.546 | 0.513 |
| $Al_2O_3$ | 0.03 | 0.05 | 0.024 | 0.028 | 0.06 | 0.018 | 0 | 0.017 | 0.014 | 0.004 | 0.015 | 0.004 |
| $Y_2O_3$ | 1.056 | 0.832 | 0.79 | 1.795 | 13.454 | 0.779 | 0.782 | 0.595 | 1.937 | 2.57 | 2.498 | 2.483 |
| $La_2O_3$ | 11.397 | 11.774 | 12.313 | 9.852 | 4.628 | 15.518 | 15.465 | 14.484 | 13.667 | 12.49 | 12.814 | 12.499 |
| $Ce_2O_3$ | 26.135 | 28.073 | 28.168 | 22.244 | 10.365 | 32.092 | 32.532 | 30.643 | 28.952 | 28.721 | 28.942 | 29.334 |
| $Pr_2O_3$ | 2.804 | 2.862 | 3.034 | 2.482 | 0.995 | 2.6 | 2.951 | 2.9 | 2.964 | 2.727 | 2.817 | 2.856 |
| $Nd_2O_3$ | 11.501 | 12.699 | 12.205 | 9.784 | 3.71 | 11.168 | 11.155 | 11.715 | 10.548 | 10.738 | 10.338 | 10.383 |
| $Sm_2O_3$ | 2.154 | 2.255 | 2.192 | 1.949 | 0.858 | 1.146 | 1.091 | 2.051 | 1.535 | 1.875 | 1.677 | 1.731 |
| $Eu_2O_3$ | 0 | 0.082 | 0.039 | 0.119 | 0.418 | 0 | 0 | 0 | 0.048 | 0 | 0 | 0.082 |
| $Gd_2O_3$ | 1.701 | 1.702 | 1.845 | 1.524 | 2.059 | 0.707 | 0.734 | 1.448 | 1.322 | 1.453 | 1.446 | 1.557 |
| $Dy_2O_3$ | 0.387 | 0.357 | 0.384 | 0.508 | 2.233 | 0.152 | 0.21 | 0.233 | 0.583 | 0.601 | 0.589 | 0.554 |
| $SiO_2$ | 1.286 | 0.929 | 0.732 | 2.977 | 5.611 | 1.005 | 0.86 | 0.336 | 0.224 | 0.709 | 0.562 | 0.56 |
| $ThO_2$ | 10.247 | 8.157 | 6.958 | 16.744 | 25.071 | 4.769 | 4.245 | 4.97 | 5.754 | 6.093 | 5.783 | 5.711 |
| $UO_2$ | 0.023 | 0.003 | 0 | 0.545 | 0.012 | 0.055 | 0.038 | 0.049 | 0.385 | 0.32 | 0.368 | 0.356 |
| $P_2O_5$ | 28.434 | 28.936 | 29.398 | 24.688 | 18.141 | 28.88 | 29.099 | 30.01 | 30.406 | 29.302 | 29.873 | 29.358 |
| $As_2O_5$ | 0.023 | 0 | 0 | 0.034 | 0 | 0 | 0.023 | 0.078 | 0 | 0.021 | 0.043 | 0.014 |
| Total | 99.396 | 100.738 | 99.944 | 98.621 | 93.673 | 99.657 | 99.96 | 100.568 | 99.921 | 99.25 | 99.428 | 99.135 |

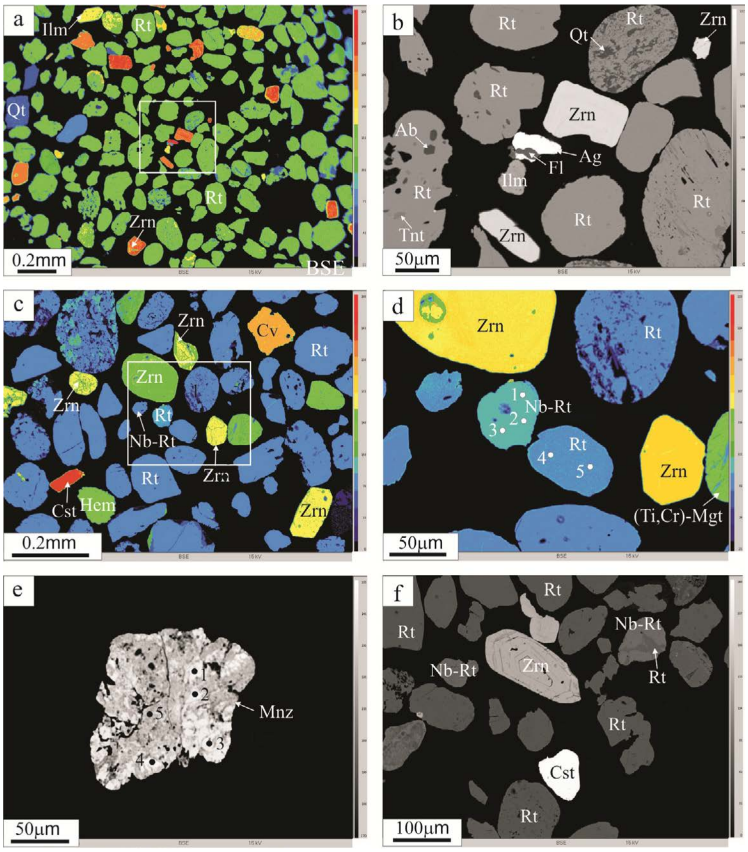


Fig. 5. The heavy minerals concentrate from the Słupsk Bank with visible well-rounded grains. Sample no. LS-K-7 a) Rutile (Rt; green) grains dominate among minerals in the heavy minerals concentrate; Zrn – zircon (orange); Ilm – ilmenite; Qt – quartz (blue). BSEI. Fragment in square enlarge on the next photo, b) Grains of rounded rutile, together with zircon (Zrn) and ilmenite (Ilm) and with single grain of native silver intercalated with fluorite (Fl). Ab – albite; Tnt – titanite; BSEI, c) BSEI in artificial colors reveals different minerals in heavy minerals concentrate; Nb-Rt – Nb rutile; Rt – rutile; Zrn – zircon; Hem – hematite; Cst – cassiterite; Cv – covellite. Fragment in square enlarge on the next photo, d) BSEI in artificial colors with visible point of SEM analyses. Zrn – zircon; Rt – rutile; (Ti, Cr)-Mgt – (Ti,Cr) – magnetite. BSEI/field 03/photo-2, e) Rounded and fractured grain of monazite (Mnz) with visible point of SEM analyses. BSEI/field 04/photo-2, e) Rounded grains of rutile (Rt), zircon (Zrn) and cassiterite (Cst). In some rutile grains are visible darker parts enriched in niobium (Nb-Rt). BSEI

Rys. 5. Koncentrat minerałów ciężkich z Ławicy Słupskiej z widocznym dobrym obtoczeniem ziarn. Próbka nr LS-K-7. a) Ziarna rutylu (Rt; zielony) dominują wśród minerałów koncentratu; Zrn – cyrkon (pomarańczowy); Ilm – ilmenit; Qt – kwarc (niebieski). BSEI. Fragment w prostokącie jest powiększony na następnym zdjęciu, b) Obtoczone ziarna rutylu wraz z cyrkonem (Zrn) i ilmenitem (Ilm) oraz z pojedynczym ziarenkiem srebra rodzimego w przeroście z fluorytem (Fl). Ab – albit; Tnt – tytanit; BSEI, c) BSEI – Obraz elektronów wstecznie odbitych w sztucznych barwach uwypukla różnice w obecności minerałów w koncentracie; Nb-Rt – Nb rutyl; Rt – rutyl; Zrn – cyrkon; Hem – hematyt; Cst – kasyteryt; Cv – kowelin. Fragment w prostokącie jest powiększony na następnym zdjęciu, d) BSEI w sztucznych barwach z widocznymi punktami analiz SEM. Zrn - cyrkon; Rt – rutyl; (Ti, Cr)-Mgt – (Ti,Cr) – magnetyt. BSEI/obszar 03/foto-2, e) Zaokrąglone i spękane ziarno monacytu (Mnz) z widocznymi punktami analiz SEM. BSEI/obszar 04/foto-2, e) Zaokrąglone ziarna rutylu (Rt), cyrkonu (Zrn) i kasyterytu (Cst). W niektórych ziarnach rutylu widoczne są ciemniejsze strefy wskazujące na domieszki niobu (Nb-Rt). BSEI

Table 5. WDS composition (in wt.%) of rutile, Nb-rutile and pirochlor grains in the heavy minerals concentrate from the Słupsk Bank (LS-K-7)

Tabela 5. Skład chemiczny (w % wag.) rutylu, Nb-rutylu i pirochloru z koncentratu minerałów ciężkich z Ławicy Słupskiej (LS-K-7) na podstawie badań na mikrosondzie elektronowej (EPMA)

| LS_K-7_area-03_photo-2 | | | | | | LS_K-7_area-07_photo-2 | | | |
|---|---|---|---|---|---|---|---|---|---|
| Formula | 1/1 | 2/1 | 3/1 | 4/1 | 5/1 | 1/1 | 2/1 | 3/1 | 4/1 |
| Weight % Oxide | | | | | | | | | |
| F | 0 | 0 | 0 | 0.004 | 0 | 2.663 | 2.66 | 2.655 | 2.681 |
| S | 0.002 | 0.021 | 0.004 | 0 | 0.002 | 0.052 | 0.053 | 0.05 | 0.06 |
| Cl | 0.014 | 0 | 0.001 | 0.005 | 0.005 | 0 | 0 | 0.023 | 0.013 |
| $Na_2O$ | 0 | 0 | 0 | 0 | 0 | 3.627 | 3.674 | 3.652 | 3.771 |
| $K_2O$ | 0.01 | 0 | 0.013 | 0.007 | 0.01 | 0.013 | 0.011 | 0.012 | 0.002 |
| MgO | 0 | 0 | 0 | 0 | 0 | 0.147 | 0.148 | 0.144 | 0.269 |
| CaO | 0.008 | 0.005 | 0 | 0.003 | 0.011 | 17.122 | 17.121 | 17.131 | 17.109 |
| MnO | 0.034 | 0.012 | 0 | 0 | 0 | 0.175 | 0.171 | 0.181 | 0.167 |
| FeO | 3.29 | 3.192 | 3.352 | 0.635 | 0.647 | 2.111 | 2.056 | 1.983 | 2.008 |
| SrO | 0 | 0.014 | 0 | 0.018 | 0.018 | 0.295 | 0.261 | 0.24 | 0.233 |
| PbO | 0.013 | 0.009 | 0 | 0.019 | 0.004 | | | | |
| $Al_2O_3$ | 0.018 | 0.036 | 0.038 | 0.099 | 0.077 | 0.118 | 0.119 | 0.137 | 0.147 |
| $Y_2O_3$ | 0 | 0.004 | 0.015 | 0 | 0 | 0.294 | 0.273 | 0.264 | 0.29 |
| $La_2O_3$ | 0.053 | 0 | 0.03 | 0 | 0 | 0.98 | 0.791 | 0.852 | 0.761 |
| $Ce_2O_3$ | 0.201 | 0.172 | 0.179 | 0.156 | 0.196 | 4.712 | 4.797 | 4.565 | 4.467 |
| $Pr_2O_3$ | 0 | 0.05 | 0 | 0 | 0.048 | 0.278 | 0.372 | 0.156 | 0.521 |
| $Nd_2O_3$ | 0 | 0 | 0 | 0 | 0 | 1.003 | 1.106 | 1.079 | 1.105 |
| $Sm_2O_3$ | 0 | 0 | 0 | 0 | 0.024 | 0.157 | 0.183 | 0.186 | 0.066 |
| $SiO_2$ | 0.025 | 0.004 | 0.013 | 0.014 | 0.041 | 0.031 | 0.017 | 0.021 | 0.022 |
| $TiO_2$ | 89.533 | 90.484 | 89.592 | 97.615 | 97.57 | 0.241 | 0.224 | 0.174 | 0.194 |
| $ThO_2$ | 0 | 0 | 0 | 0 | 0.01 | 0.039 | 0.056 | 0.045 | 0.052 |
| $UO_2$ | 0.005 | 0 | 0 | 0.001 | 0.023 | 0 | 0 | 0.005 | 0 |
| $P_2O_5$ | 0.008 | 0.012 | 0.016 | 0 | 0 | 0.051 | 0.008 | 0 | 0.025 |
| $Nb_2O_5$ | 5.662 | 5.418 | 5.773 | 0.917 | 0.912 | 63.224 | 63.838 | 63.638 | 63.429 |
| $Ta_2O_5$ | 0.351 | 0.133 | 0.408 | 0.056 | 0.04 | 0 | 0.048 | 0.102 | 0.259 |
| Total | 99.226 | 99.565 | 99.434 | 99.548 | 99.64 | 97.335 | 97.987 | 97.295 | 97.65 |

Microscope and microprobe studies showed the domination of rutile in the ŁS(Zr) heavy minerals concentrate sample. Rutiles constitute almost 65–70% of all grains (Fig. 5a). Rutiles have sizes ranging from 50 to 150 μm in diameter, rounded edges and they are commonly intercalated with quartz and ilmenite or less frequently with xenotime or zircon. The rutile variety also appears with a high admixture of niobium (5–6 weight % of $Nb_2O_5$; Table 5). Nb-bearing rutile's are generally a bit smaller (approx. 50 μm in diameter) in relation to common rutile grains (Fig. 5c–5d, 5f). Albite or titanite inclusions have been found within the larger grains of rutile (about 100 μm in diameter) (Fig. 5B). The zircon grains are the second component (a dozen percent share) in the heavy minerals concentrate. Zircons generally have sizes ranging from 70 to 130 μm in diameter. Single grains of copper minerals (covellite and cuprite), cassiterite (Fig. 5c, 5f) as well as native silver intercalated with fluorite appear in the concentrate (Fig. 5a, 5b). Monazite found in concentrate revealed an usually high concentration of LREO (sum >50 weight %; Table 4) and moderate $ThO_2$ admixtures (7–10 weight %). On the other hand, thorium and yttrium enrichments (maximum contents of $ThO_2$ and $Y_2O_5$ ~25 and 13.4 weight %, respectively) are poorer in LREEO (sum 30–40 weight %) monazite.

In the heavy minerals concentrate well-rounded grains of magnetite (80–200 μm in diameter), ilmenite and single grains of xenotime (of sizes 70–110 μm in diameter) are present also as well as strongly altered grains of monazite (up to 150 μm in diameter; Fig. 5e; Table 4). Monazite was also found in the form of inserts in zircon grains. Xenotime has

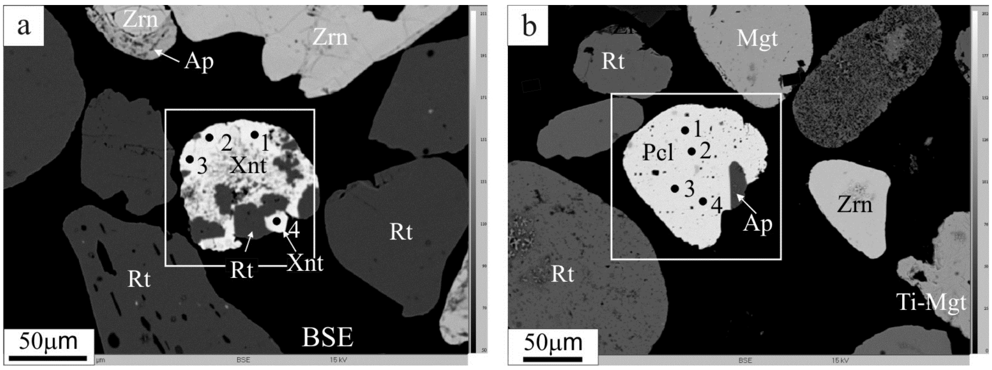


Fig. 6. The heavy minerals concentrate from the Słupsk Bank with visible well-rounded grains of different minerals. Sample no. LS-K-7
a) Well-rounded grain of xenotime (Xnt; with visible point of SEM analyses) intercalated with rutile (Rt). The one of the zircon (Zrn) grain with apatite (Ap) rim is visible. BSEI/field 06/photo-1, b) Grains of rounded pyrochlore (Pcl) with insert of apatite (Ap). Ti-Mgt – Ti-magnetite; BSEI/field 07/photo-2

Rys. 6. Koncentrat minerałów ciężkich z Ławicy Słupskiej z widocznym dobrym obtoczeniem różnych minerałów. Próbka nr LS-K-7
a) Dobrze obtoczone ziarno ksenotymu (Xnt; z widocznymi punktami analiz SEM) przerastające się z rutylem (Rt). Widoczne jest jedno z ziarn cyrkonu (Zrn) z otoczką apatytu (Ap). BSEI/obszar 06/foto-1,
b) Zaokrąglone ziarna pirochloru (Pcl) z wrostkami apatytu (Ap). Ti-Mgt – Ti-magnetyt; BSEI/obszar 07/foto-2

a high contents of yttrium ($Y_2O_3$, 38–40.5 weight %) and HREEO (sum >25 weight %; Table 3). Xenotime may form intercalation with rutile (Fig. 6A). In addition, a strongly rounded single grain of pirochlor (with a diameter of approx. 100 µm) and a high content of Nb ($Nb_2O_5$ 63–64 weight %; Table 5), and low admixture of Ce and La (c.a. 6–7 weight % of LREEO) with the apatite inserts were identified (Fig. 6b).

### 3.3. Hel Peninsula

As a result of the ICP-MS chemical analysis, the presence of rare earths represented mainly by the lanthanides and another elements such as thorium, yttrium and scandium was found in one of the samples (Table 1). In the shore sands sample (# He2) from the trench (Fig. 3B) the significant enrichment in the light lanthanides group with a high proportion of cerium, and then lanthanum and neodymium is characteristic. The concentration of yttrium is also noteworthy. Besides, part of the thorium is also high in this sample (147.4 ppm). The sum of REE in the first sample (#He1) from this area is very low (40 ppm). In turn, the sum of REE is much higher in the second sample – 0.14 weight %. In this sample, the light lanthanides also dominate. The cerium concentration reaches c.a. 0.6 g/kg, and lanthanum and neodymium concentration exists in the amount of 0.3 and 0.26 g/kg, respectively. The content of neodymium and yttrium is in the range of 100–250 mg/kg. Components of the heavy lanthanides subgroups are in the range from several to twenty some mg/kg (for example Dy). In comparison with a beach sands sample, (He1) collected from the surface has a significantly increased concentration of REE (>40-times). And if we compared this sample to the other 3 Baltic marine sand samples from the Odra Bank (Table 1), we can notice that He2 sample enrichment in REE is from 5 to 15 times greater. The exceptions are ŁO(Zr) and ŁS(Zr) samples of heavy minerals concentrates which contain total sum of rare earths from 4 to 6 times higher than in the He2 sample. The comparison of REE content in samples to chondrite (Fig. 7) points to their considerable enrichment in LREE (3 samples are enriched more than 1000 times) and much lower in HREE (at the level of about 100-times). In all the samples examined by ICP-MS, the total sum of REE ranges from traces (40 ppm) to 0.9% (Table 1).

The distribution of rare earth elements content in the all samples tested by ICP-MS method indicate a predominance of light lanthanides, including cerium, which remains in close correlation with the presence of grains of monazites. Monazites have been found up to a few percent of total volume of heavy minerals concentrate. The chemical composition of monazites revealed during microprobe analyses indicates a high contents of $Ce_2O_3$ (max. 32.5 weight %), and of $Nd_2O_3$ (11–13 weight %) and moderate contents of $La_2O_3$ (max. 15.5 weight %). In turn, relatively high yttrium content in the heavy minerals concentrate is due to the presence of xenotime. Increased contents of neodymium (0.017%) and thorium (0.0008%) were also found in this sample. The neodymium content is strongly correlated with the presence of pirochlor and Nb-bearing rutile in concentrate grains. On the other

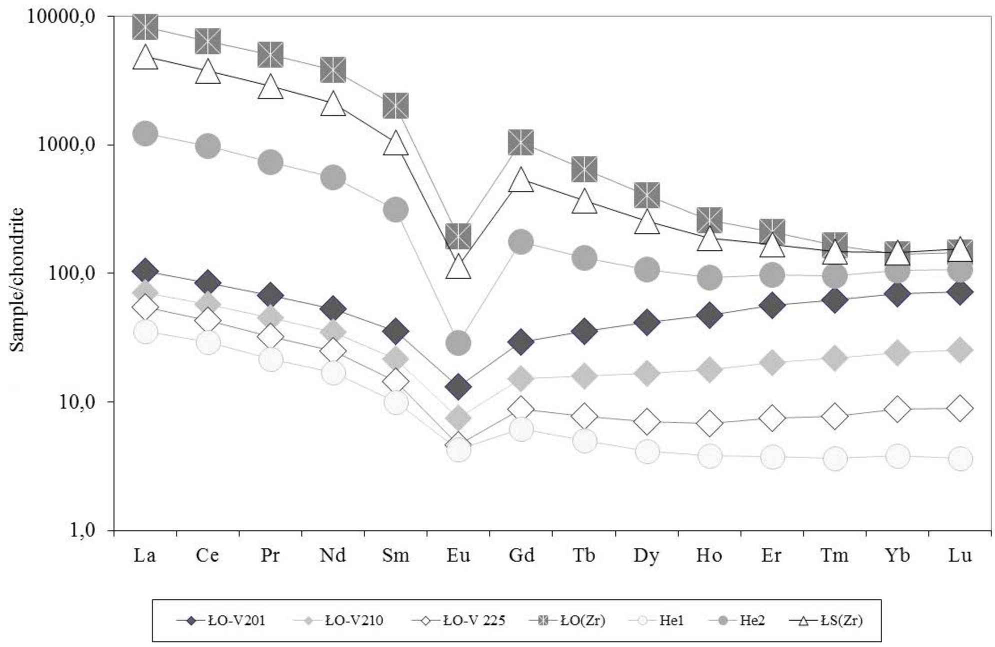


Fig. 7. The characteristics of the rare earths in the samples of marine sands and zircon concentrates [samples # ŁO(Zr) and ŁS(Zr)] from the Baltic Sea area normalized to chondrite (after McDonough and Sun 1995)

Rys. 7. Znormalizowany wykres logarytmiczny koncentracji REE w próbkach piasków i koncentratów cyrkonu [próbki nr: ŁO(Zr) i ŁS(Zr)] z regionu Morza Bałtyckiego w stosunku do zawartości w chondrycie (wg McDonough i Sun 1995)

hand, the enrichments in thorium are strongly correlated with the appearance of Th-bearing apatite and monazite in concentrate grains.

## Summary

The rare earth elements results of pilot analytical work (ICP-MS methodology) in the marine sands of the Baltic Sea presented in the article have shown that some heavy minerals concentrate samples from the Odra and Słupsk Banks as well as in the one sample from the Hel Peninsula (16.6 km stretch of beach) are reaching a concentration that may be of interest in terms of economy. The results of this investigation confirmed the dependence of the REE concentration with the percentage of heavy minerals content in the marine sands. In the examined samples, it is the vast preponderance of LREE among the rare earths. The highest concentration mainly is achieved by cerium and almost two times lower by lanthanum. The total REE content in the considered 3 richest samples is from c.a. 0.14% (He2 sample from Hel Peninsula) to 0.9% (LO/Zr; heavy minerals (zircon) concentrate from the Odra Bank).

Microprobe investigations indicate that monazite is the main carrier of LREE in marine sands, and a high yttrium contents is correlated with the appearance of xenotime among the heavy minerals. Moreover, pirochlor and Nb-bearing rutile are responsible for a high neodymium concentration. Thorium is considered as strongly correlated with the appearance of Th-bearing apatite and monazite in concentrate grains. The enrichments in REE concentration is accompanied by the high contents of Th (150–900 ppm).

The previous recognition of heavy mineral resources in the Baltic sands is limited to a small area on the Odra and Słupsk Banks. More research should be done in the prospective areas situated to the North-East from the already documented placer fields with estimated resources on the Odra Bank. Furthermore, new work should be carried out in the tentatively identified areas on the Słupsk Bank, as well as along the underwater slope (paleo-slope) and on the beaches of the Hel Peninsula. Research on the minerals identification of rare earths and on the technology of recovery of REE-bearing minerals from heavy minerals concentrates should be carried out in parallel with the documentary work. This source of LREE from the heavy mineral concentrates received from the Baltic sandbanks may be interesting for recovery by the domestic economy. The presence of LREE, especially cerium, in heavy minerals concentrate is valuable due to its use in the production of catalytic converters or metal alloys. In addition, lanthanum, which is used in vehicles with hybrid drive (batteries), x-ray film or catalyst in the process of refining crude oil is present in the concentrate. In turn, neodymium is consumed during the production of strong neodymium magnets as well as for the fabrication of lasers.

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## PILOTAŻOWE BADANIA PIERWIASTKÓW ZIEM RZADKICH W PIASKACH MORSKICH BAŁTYKU WZBOGACONYCH W MINERAŁY CIĘŻKIE

Słowa kluczowe

pierwiastki ziem rzadkich, minerały ciężkie, piaski morskie, paleo-mierzeje, Morze Bałtyckie

Streszczenie

Przeprowadzono pilotażowe prace nad koncentracją REE w piaskach bałtyckich za pomocą metodyki ICP-MS oraz mikrosondy elektronicznej (CAMECA SX-100). Analizy chemiczne składu jakościowego i ilościowego pierwiastków ziem rzadkich w próbkach piasków z koncentratów minerałów ciężkich z Ławicy Odrzanej oraz z Ławicy Słupskiej jak również z wkopu na plaży na Półwyspie Helskim (16,6 km plaży wybrzeża) osiągają zawartości REE, które mogą być interesujące pod względem surowcowym. Wyniki oznaczeń potwierdzają zależność koncentracji REE od procentowej zawartości minerałów ciężkich w osadach piasków morskich. Wskazują ponadto na monacyt jako główny wśród minerałów nośnik REE. W zbadanych próbkach koncentratów minerałów ciężkich oraz w próbce z Półwyspu Helskiego jest zdecydowana przewaga LREE. Najwyższe koncentracje osiąga głównie cer, a prawie dwukrotnie niższe lantan. Suma REE w wyżej wymienionych najciekawszych pod względem zawartości REE próbkach mieści się w zakresie od około 0,14% (wkop na plaży) do

około 0,9% (koncentrat z Ławicy Odrzanej). Wysokiej koncentracji REE towarzyszy wysoka zawartość Th (900–150 ppm). W próbkach koncentratu minerałów ciężkich pojawia się również neodym (0,1–0,17% Nd), którego obecność jest związana z pojawianiem się pirochloru oraz Nb-rutylu.

Konieczne jest systematyczne rozpoznanie zasobów minerałów ciężkich w piaskach bałtyckich. Dokładniejszymi badaniami powinny być objęte obszary perspektywiczne położone na północny wschód od pól złożowych objętych dokumentacją zasobową „Ławica Odrzana", wstępnie rozpoznane obszary na Ławicy Słupskiej oraz podwodny skłon (paleo-mierzeja) Półwyspu Helskiego.

## RARE EARTH ELEMENTS PILOT STUDIES OF THE BALTIC SEA SANDS ENRICHED IN HEAVY MINERALS

K e y w o r d s

rare earth elements, heavy minerals, marine sands, paleo-shoals, Baltic Sea

A b s t r a c t

The carried out pilot work on the concentration of rare earth elements (REE) in the Baltic marine sands from the Odra and Słupsk Banks showed that in some places their accumulations are quite interesting in terms of the placer deposits and may be the subject of an interesting prospecting project. The results of ICP-MS and electron microprobe (CAMECA SX-100) investigation confirm the close relationship of REE concentration to heavy minerals content in the sediments of marine sands. It is indicated, in addition to monazite, as a primary mineral carrier of rare earth elements. The vast preponderance of light REE is noted in the samples of heavy mineral concentrates from the Odra and Słupsk Banks as well as in the beach sand sample from the Hel Peninsula. The highest concentrations are achieved mainly by cerium and almost two times less by lanthanum. The total REE in the most interesting considered samples range from c.a. 0.14% (trench on the beach) to 0.9% (heavy minerals concentrate from the Odra Bank). The high contents of REE are accompanied by a high concentration of Th (900–150 ppm). Neodymium (0.1–0.17% Nd), whose presence is associated with the presence of pyrochlore and Nb-rutile also appears in the heavy minerals concentrate samples. It is necessary to systematically identify heavy minerals resources in the Baltic sands. More detailed research should cover the prospective areas situated to the North-East from the documented placer fields of the Odra Bank, as well as tentatively identified areas of the Słupsk Bank and submarine paleo-slope of the Hel Peninsula.