nvestigation of the REE abundance and distribution in thermal and mineral waters of Poland.

Acronim: THERMREE

The Rare Earth Elements (REE) or rare earth metals are commonly defined as a group of fifteen elements comprising the lanthanides series in the periodic table: lanthanum (La), cerium (Ce),

praseodymium (Pr), neodymium (Nd), promethium (Pm), samar ium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu) (Fig.1). Additionally, according to IUPAC, scandium (Sc) and yttrium (Y) are considered REEs because they exhibit similar chemical properties and tend to occur in the same ore deposits as the lanthanides.

The uniqueness and importance of the REE in geological systems stem from similarity of their chemical properties. They are lithophile elements and occur together naturally because all are trivalent (except for Ce+4 and Eu+2 in some environments) and have similar ionic radii which allow for liberal substitution of the REE for each other into various crystal lattices. This substitution accounts for their wide dispersion in the earth's crust and the characteristic multiple occurrences within a single mineral. On the other hand, ample evidence has been provided that the REE can be significantly mobilized during weathering, alteration and diagenesis processes and transferred into aquatic environment. Groundwaters usually demonstrate REE patterns that closely reflect the REE patterns of the rock through which they flow. Such similarities between groundwater and aquifer rock REE patterns suggest that REE may be useful tracers of groundwater – aquifer rock interactions. Moreover, many studies have already demonstrated the utility of the REE as chemical tracers of numerous geochemical processes of primary importance in studying various hydrogeological systems, e.g. dissolution-precipitation reactions in the aquifer including those along flow paths, groundwater and surface water mixing, weathering, biogeochemical redox processes, adsorption processes, etc.

On the other hand, the versatility and specificity of the REE has given them a great technological, environmental and economic importance. The diverse nuclear, metallurgical, catalytic, electrical, magnetic and optical properties of the REE have led to an ever increasing variety of applica¬tions. They are critical to the new „clean" energy technologies, including wind turbines, electric car batteries and energy-efficient lights, which help to reduce CO2 and other emissions. Their uses range from mundane (catalysts, lighter flints, glass polishing) to high-tech (phosphors, lasers, magnets, batteries, magnetic refrigeration) to futuristic (high-temperature superconductivity, safe storage and transport of hydrogen for a post-hydro¬carbon economy). The REE have a wide variety of defence applications (missiles and "smart" bombs, lasers as rangefinders, target designators, and target interrogators, high-power sonars, radar systems, permanent magnets in aircrafts, computers). They have been also employed in agriculture as fertilizers and medicine as powerful magnets in magnetic resonance imaging or contrast agents). These elements help make many technologies perform with reduced weight, emissions, and energy consumption, and give them greater efficiency, performance, miniaturization, speed, durability, and thermal stability.

Despite the vast literature and numerous studies of REEs geochemistry reported for various regions in the world, Poland is a truly white spot, where the REE in the groundwater systems have never been deeply studied, and there is not any scientific contributions to this subject. The present project is the first in Poland which directly deals with the determination, analyses and application of the REE in mineral and thermal waters that are encountered in various hydrogeological systems.

The main purpose of this project is (I) to determine the distribution and systematic changes of the REE concentration in thermal and mineral waters of Poland, and (II) application of the REE fractionation in water-rock system as a geochemical probe to study various biogeochemical and minero-chemical processes occurring in aquifers, groundwater reservoirs, or along groundwater circulation paths.

The mineral and thermal waters in various parts of Poland are the subject of the proposed research. All of them belong to several regional hydrogeological systems which differ among each other in water chemistry and origin as well as aquifer lithology, stratigraphy and tectonic style. For the purpose of this study the representative groundwaters and aquifer rocks of the following hydrogeological regions will be taken into account: (1) mineral and thermal waters of the flysch Carpathians, (2) thermal waters of the Podhale Basin, (3) mineral and thermal waters of the Sudetic region, (4) mineral and thermal

waters of the Polish Lowlands: Paleozoic and Precambrian Platforms (see the map in Fig. 1)
Our project embraces the determination of the total amount of REE present in the groundwater samples and in the aquifer rocks collected in different regions of Poland and having different origin. Only chemical analysis carried out for the appropriate water-rock couples may supply information about interaction of the groundwater with aquifer host rocks and allows to understand the behavior of REE depending on specific hydrogeological and thermal conditions in the aquifers studied.

Methodologically, the project includes the determination of content and distribution of REE in groundwaters and aquifer rocks. An overall about 80 samples of water and about 120 samples of aquifer rocks (mainly core samples) are going to be taken to analysis. The samples of water will be subjected to: (a) chemical analyses, including macro-, micro- and trace elements with application of ICP MS and HPLC techniques, and (b) isotopic analyses, including O and H of waters, O and S of dissolved sulfates, and C, O, H and S of selected gas phases (e.g. H_2S, CO_2 or CH_4). The REE abundance in natural waters usually is in the range of nmol/kg to even below pmol/kg. Therefore, to reach such level of detection the application of the pre-concentration system is indispensable. This new analytical technique (i.e. SeaFAST-ICP-MS system) is held since march 2015 by the Central Chemical Labolatory of PIG-PIB (the partner in the consortium) especially for the purpose of this project. The samples of rocks will be subjected to detailed chemical analysis (as bulk samples) including REE content, as well as to detailed mineralogical studies with a application of SEM-EDS (-WDS) and laser ablation (LA-ICP-MS) for determination of main and accessory mineral phases and their REE content.
The realization of the project has a tremendous national significance: up to date in Poland similar investigations of the REE in groundwaters (especially the mineral and thermal ones) have never been done before, and no serious data are published in this subject. Therefore, the realization of the project will initiate the development of new discipline in Poland – the geochemistry of REE. The involvement of two doctoral students will also enhance the impact in this area.
The application of the REE distribution as the new (i.e. not used so far in Poland) indicator of the water-rock interactions, dissolution/precipitations processes, groundwater origin and mixing, will undoubtedly bring the new data allowing clarification, verification, systematization and better recognition and understanding the complex hydrogeological systems of mineral and thermal waters in Poland.
The realization of the project will directly contribute to the development and implementation of new technique of REE determination in waters of different origins, chemical compositions and salinities. Thus, the main technological obstacle on the way of wider application of REE to study the groundwater systems in Poland will be eliminated.
For the successful realization of the proposed research project the scientific consortium has been established including the Institute of Geological Sciences of Polish Academy of Sciences (ING PAN) and the Polish Geological Institute – National Research Institute (PIG-PIB). At the same time, the interdisciplinary team of experienced scientists from both institutions has been appointed. The scientific team consists of six researchers (having documented experience in the field of hydrogeology, isotope hydrogeochemistry, geochemistry, analytical chemistry, mineralogy and petrography), two PhD students, technical personnel (6 persons) and two scientific advisors – i.e. known scientists at the Professor level.