

TRACKING DOWN RARE-EARTH ELEMENTS

Electron microprobe laboratory at the Faculty of Geology at the University of Warsaw and the field emission electron probe micro analyzer CAMECA SX Five FE (operated by Dr. Petras Jokubauskas) for precise measurements of chemical compositions of solids of up to 0.001 mm diameter


**Prof. Bogusław
Bagiński**

works at the Faculty of Geology at the University of Warsaw, where he heads the Department of Geochemistry, Mineralogy, and Petrology. He studies accessory minerals, in particular those rich in rare-earth elements. In 2020, he was awarded the prestigious Stanisław Staszic Prize, funded by the Polish Academy of Sciences.
b.baginski1@uw.edu.pl

Rare-earth elements have countless applications in electronic devices that use state-of-the-art technologies. Experimental research is aimed at making it easier to find them, by predicting their behavior in the processes that form mineral ores.

Bogusław Bagiński

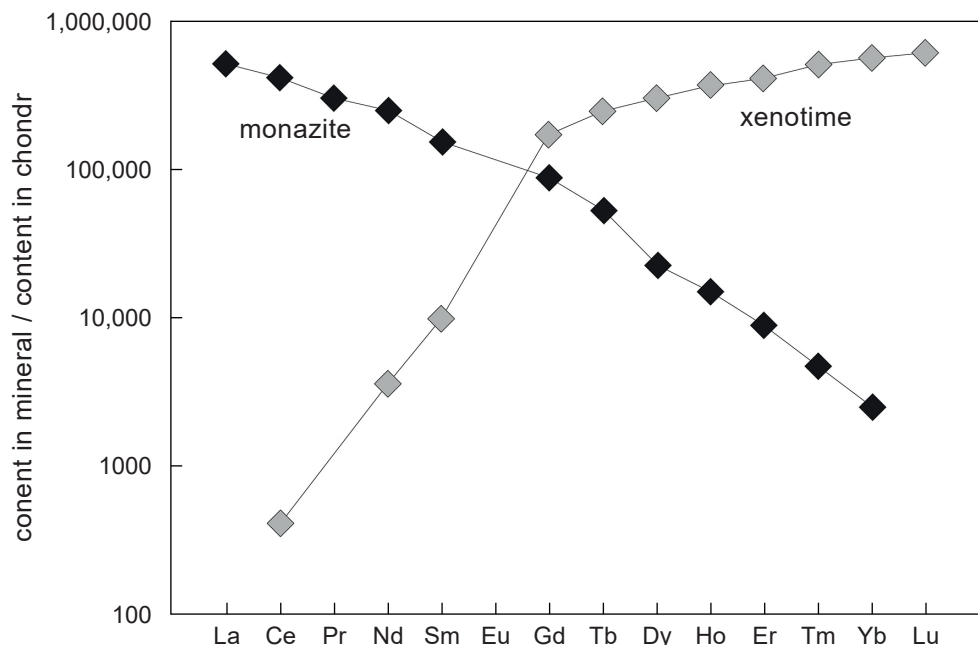
Faculty of Geology,
University of Warsaw

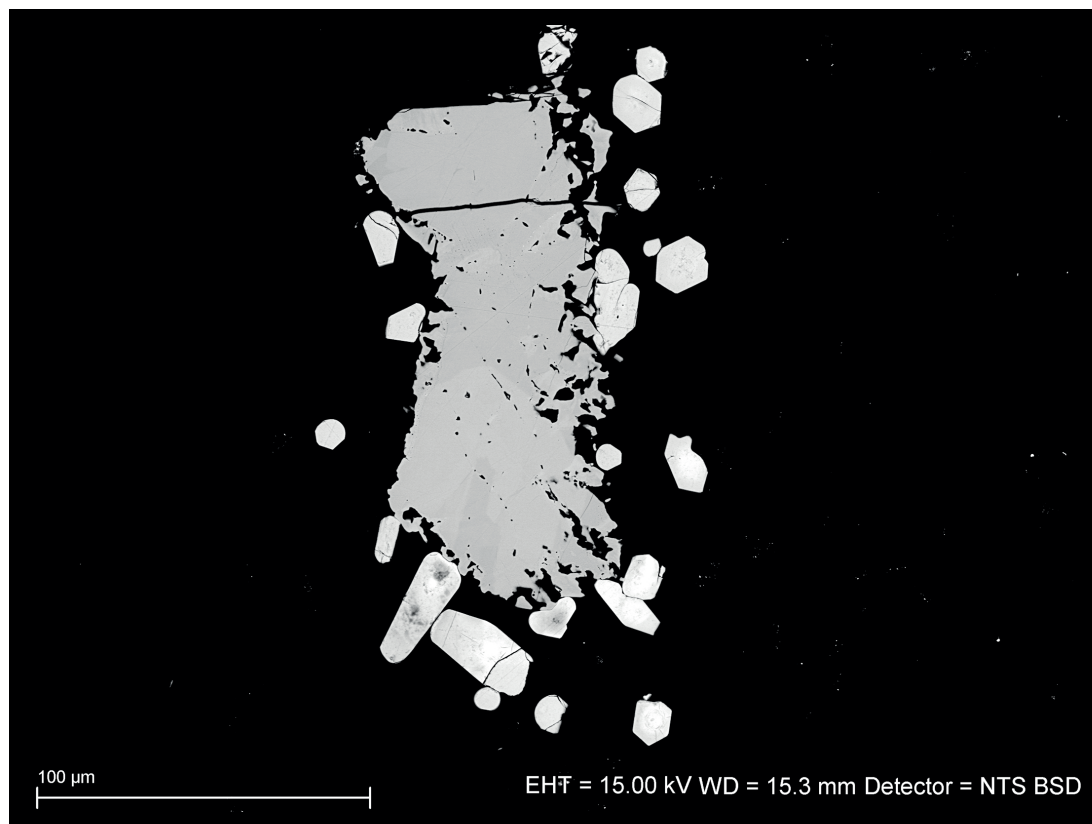
With the advance of state-of-the-art technologies, rare-earth elements have become indispensable in our everyday lives. They are used, for example, in the liquid crystal displays of mobile phones and TVs, in the magnets in our speakers and headphones, in computer and smartphone storage, in engines, generators and catalysts, making them some of the most essential raw materials in technologically-advanced everyday objects. But where do they occur, and where can minable deposits be found?

In spite of their name, rare-earth elements (REEs) are not particularly rare in the Earth's crust. They are a group of 17 different elements: scandium (Sc), yttrium (Y), lanthanum (La), cerium (Ce), praseodymium

(Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). The most common – La, Ce, and Nd – occur in quantities similar to more familiar elements such as chromium (Cr), nickel (Ni), and zinc (Zn). The average content of the rarest REEs in the lithosphere is approx. 200 higher than that of gold. However, unlike gold, they do not appear in the form of nuggets, containing almost 100% of the pure element. Rather, they tend to concentrate in “accessory minerals” which occur in rocks in low amounts (fractions of a percent). The REE content in certain accessory minerals may exceed 50% of their mass, making them the main component. Such minerals frequently contain several REE at the same time. The majority of accessory minerals containing REE (such as monazite, britholite, and bastnäsite) mostly contain light REEs (La, Ce, and Nd), while others, such as xenotime, tend towards heavier REEs, such as Lu, Yb, and Y. This depends on the crystal structure and chemical composition of each mineral.

Diagram showing typical content of REE in monazite (mainly light REEs) and xenotime (mainly heavy REEs). The logarithmic scale indicates the ratio of the content of each particular element found in the given mineral, to the content of that element found in chondrite





BSE scanning image from an electron scanning microscope showing the results of an experiment during which fluoride-rich solutions partially dissolved chevkinite-(Ce) (large and grey, in the center) and the formation of gagarinite-(Ce) (the surrounding pale small crystals)

Occurrence

Processes occurring in rocks and minerals over millions, even billions of years may lead to the accumulation of certain elements, elevating their levels by a factor of a million. This has important implications, since these formations are the most desirable to mine.

Another important, practical aspect of searching for and extracting REEs, in particular obtaining them from ore, is the way they are bound in the mineral structure. At issue is the amount of energy required to extract the desired element. Accessory minerals containing high volumes of REEs may form compounds (minerals) such as silicates, phosphates, oxides, and carbonates. Extracting REEs is most straightforward when they have the loosest bonds within the mineral structure, in this instance as carbonate minerals. Such deposits are not common; the largest and the most important source of REEs is Bayan Obo in China near the border with Mongolia, which mainly contains carbonate deposits. Its genesis is highly complex and not fully understood. In summary, its formation involved hydrothermal solutions, generated deep underground during metamorphic processes turning dolomite (carbonate) rock into magnesium/calcium rock. The composition of these solutions was key, since only some are able to liberate REEs from the mineral structures.

GLOSSARY

Accessory minerals

A minor component of the assemblages of minerals comprising a rock. Usually occurring as small crystals visible under a microscope.

Hydrothermal solutions

Aqueous solution saturated with gases and organic and inorganic compounds soluble under very high temperatures and pressures, penetrating rocks through microcracks.

Metamorphic processes

Processes occurring under high temperatures and pressures triggering changes in a rock (without melting it) by restructuring its mineral, chemical, and textural composition.

High field strength elements (HFSE)

These are broadly defined as elements with small radius and high cationic charge. They tend to accumulate in the final stages of magma evolution, leading to a restructuring of the composition of magma from ultra-alkaline, typical of the upper zones of the Earth's mantle, into rocks rich in silica and alkali elements (Na, K). This occurs as a result of numerous processes deep beneath the Earth's surface occurring over periods up to millions of years.

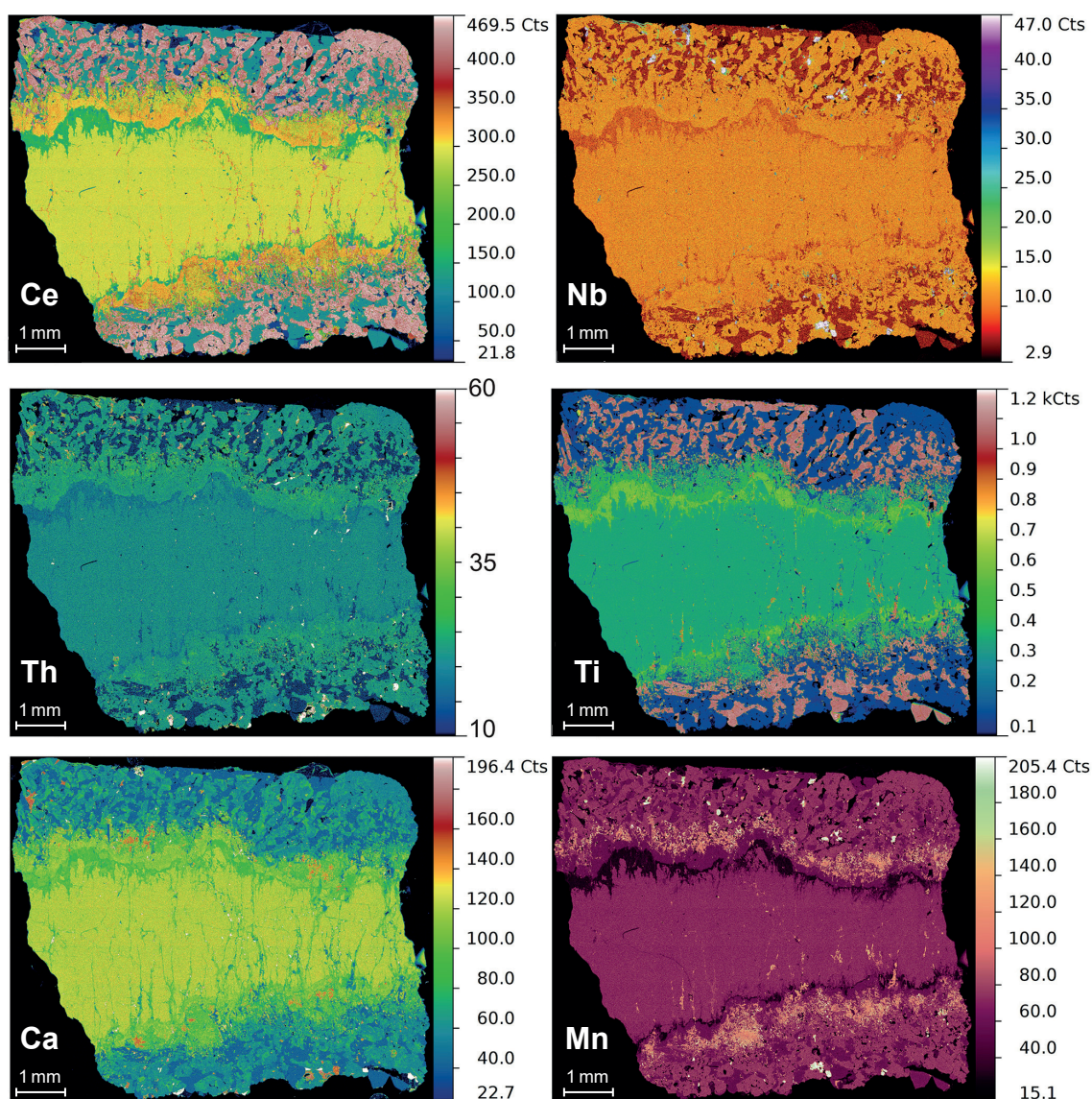
Pegmatite

A type of igneous rock containing large and very large crystals (up to several meters). Usually associated with the final stages of crystallization of acidic magma, when large volumes of residual solutions are able to crystallize as lodes or caverns.

Mineral paragenesis

Complexes of minerals with a common origin found in a rock. For example, following crystallization granite comprises minerals such as quartz, feldspar, and mica crystallized from the same magma alloy. After a period, hydrothermal solutions reacting with the rock result in the formation of other minerals, leading to a new paragenesis.

Distribution of the concentration of selected elements in a sample of a transformed chevkinite crystal based on EDS spectra using a scanning electron microscope. The color scale on the right corresponds to the changing concentration of the element. For example, higher Ce concentrations are shown as pink-brown zones, with dark blue corresponding to the lowest concentrations



Understanding the processes whereby REEs become mobilized and concentrated is one of the main goals of research into deposit formation. Such research is ongoing at the Faculty of Geology at the University of Warsaw as part of a collaboration with the GeoForschungsZentrum laboratories in Potsdam; the goal is to elucidate the mechanisms that govern the behavior of REEs during hydrothermal processes. The main object of interest is an accessory mineral known as chevkinite.

Fluids

Chevkinite group minerals (CGMs) are accessory minerals; Ti, Fe, and Ca silicates contain up to 50% REEs and significant quantities of high field strength elements (HFSEs), such as Zr, Nb, and actinides. They are relatively common in nature; we know of hun-

dreds of occurrences of CGMs all over the globe. It is notable that chevkinite group minerals have the highest number of different elements which can bind to its crystal structure, with 56 having been identified so far.

The behavior of CGMs – that is, their susceptibility to enter into reactions under the influence of hydrothermal fluids – has a major impact on REE mobility, as is the case for other REE-rich minerals such as monazite, xenotime, apatite, allanite, and titanite. In nature, such processes occur under metamorphic conditions, most commonly a few kilometers below the surface where temperatures reach up to 600°C. Understanding these processes and their mechanisms helps us explain the origins of some of these deposits. Research into the impact of hydrothermal fluids on CGM, conducted in Warsaw, has allowed us to recreate several sequences (different models) of their transformation. This is due mainly to differences in

the chemical composition of the fluids, with different concentrations of components such as fluoride, chlorine, carbon dioxide, and hydroxyl and sulfate groups. Also relevant are temperature changes and the volatility of oxygen in the system. Different associations of the products of the transformations give rise to different “behavioral models” of REEs, HFSEs, and actinides. They may be bound in the transformation products or eliminated from the system. Such research usually lacks direct data on fluid composition, which means the information must be generated indirectly, e.g. based on phases which are products of the fluid activity (carbonates, fluorides, chlorides, etc.). Observations of textures which arise during the reactions are also extremely revealing. This is especially clear when observing samples under a scanning electron microscope.

For example, observations of the decay of chevkinite-(Ce), found in alkaline pegmatites in the granite of the Vishnevy Range of the Ural Mountains in Russia, reveal the mechanism of formation of a new complex of minerals comprising bastnäsite (carbonate-fluoride), ilmenite (titanium-iron oxide) and columbite (iron and niobium oxide). There is also quartz and some calcite. The process occurs in the presence of solutions rich in carbon dioxide and fluoride via several complex intermediate steps.

It is worth noting that one of the new minerals to be formed – bastnäsite-(Ce) – is the most important source of light REEs found in the richest REE deposits, including Bayan Obo in China.

Depending on the conditions and chemical composition of hydrothermal solutions, other processes may occur. Fluids may distribute REEs into different zones of the rock mass or eliminate them from the system altogether to be deposited elsewhere, which has major consequences on the formation of deposits of these elements.

In order to establish the temperature and pressure conditions of these processes, we need highly precise analytical data, such as the chemical composition of the mineral phases being formed. This is achieved using an electron microprobe. Using precise measurements of the concentrations of selected elements in certain reaction zones, we can determine the paths and range of migration of individual elements (only within the microzone of a given sample, whose diameter does not exceed 1 inch).

It turns out that REE mobility is largely dependent on the composition of hydrothermal fluids. We have been able to document a major role played by fluorine ions in many natural systems: they effectively free light REEs from silicate and phosphate minerals, leading to the formation of more valuable carbonate-fluoride compounds, both in terms of LREE content and ease of extraction.

Achievements

In order to carry out a complex investigation of the mechanisms of the hydrothermal transformation of chevkinite, we have conducted a series of experiments at the hydrothermal laboratory at GeoForschungsZentrum in Potsdam. By carefully selecting the temperature and pressure and the chemical composition of hydrothermal fluids and substrates, we aimed to replicate natural mineral paragenesis. While the process cannot be replicated fully, since it is impossible to consider all possible variables and reagents taking part in natural reactions, we hope to recreate conditions supporting the formation of different secondary phases arising from chevkinite-(Ce) and releasing REEs, which in turn build new minerals (carbonate-fluorides and phosphates) that are even richer in REEs and with a structure more suited to REE extraction. The results of subsequent experiments are corrected

In one of our first experiments using fluoride-rich fluids, we obtained a very rare mineral which has only been found at a single site in nature: gagarinite-(Ce).

by adjusting selected parameters (pressure, temperature, composition of fluids and substrates), and the results are analyzed again using scanning electron microscopes and microprobes to provide new optimized parameters for subsequent experiments. This may appear to be a tedious, routine process, but in reality it can spring some surprises. In one of our first experiments using fluids rich in fluoride, we obtained a very rare mineral which has only been found at a single site in nature. The mineral is gagarinite-(Ce) – a fluoride of REEs and sodium, discovered in an alkaline igneous complex at Strange Lake in Canada. What is the significance? For us it is an important discovery, since the parameters used in our experiments correspond directly to those which support the natural formation of gagarinite-(Ce), which is why we obtained this particular mineral and not another. This means we are able to posit the conditions of the formation of paragenesis and deposits. Our research continues, and we are hoping for many similar surprises with new, previously undescribed minerals.

Our work is made possible by the financial support from Poland's National Science Centre (NCN), project no. 2017/26/M/ST10/00407.

Further reading:

Bagiński B., Macdonald R., Dzierżanowski P., Zozulya D., Kartashov P.M., Hydrothermal alteration of chevkinite-group minerals. Part 1. Hydration of chevkinite-(Ce), *Mineralogical Magazine* 79, 2015.

Macdonald R., Bagiński B., Belkin H.E., Stachowicz M., Composition, paragenesis and alteration of the chevkinite group of minerals, *American Mineralogist* 104, 2019.

Verplanck P.L., Hitzman M.W., Rare Earth and Critical Elements in Ore Deposits, <https://pubs.geoscienceworld.org/segweb/books/book/1998/Rare-Earth-and-Critical-Elements-in-Ore-Deposits>.