

Substitutions of rare earth elements and U in lead apatite $Pb_5(PO_4)_3Cl$

Rare earth elements (REE) are considered as critical materials since they are particularly used in the energy sector and many new electronic and advanced components such as fuel cells, mobile phones, displays, hi-capacity batteries, permanent magnets for wind power generation, green energy devices, LED-lights etc. Over the last few years the problem of REE availability has risen significantly, particularly in Europe, since China has achieved a monopolistic role in all segments of the REE value chains. REE-rich apatites, associated with iron ores in Europe and other parts of the world, are being disposed in large quantities rather than being recovered and reused due to lack of technologies of REE recovery. Also, apatite is the main source of phosphate fertilizers and phosphoric acid. However, most REE associated with apatite is lost during production processes due to poor and expensive REE recovery technologies.

Published analyses of over 150 samples of various natural lead apatites indicate that they enrich REE and U up to a factor of 10^6 particularly with respect to the solutions they precipitated from in the oxidation zone of mineral deposits. This is a very significant discovery, but the importance of this discovery in geochemistry and technology has not yet been recognized. To date, this is also the only published material on the presence of REE and U in lead apatites. Our knowledge on the presence of REE in lead apatites, for example in pyromorphite $Pb_5(PO_4)_3Cl$ is close to zero. This is particularly important in terms of natural environments (mineral-water interactions) and of material science and future applications of Pb-apatites in remediation of radioactive waste or development of REE recovery technologies.

Therefore, we propose to run a project in which for the first time a quantitative characterization of the mechanisms of incorporation, the quantity, and structural position of REE and U in pyromorphite $Pb_5(PO_4)_3Cl$ will be investigated upon precipitation from aqueous solutions. The overall purpose of this research is to accelerate scientific progress towards meeting critical elements challenges and to put Polish scientific research in this field on a much broader, international level. The goals will be accomplished by experimental research: precipitation of pyromorphite at the presence of dissolving natural calcium apatites containing REE as well as synthesis of pyromorphite from the solutions containing REE or U. This will be followed by careful quantitative analysis of solutions and characterization of solids in terms of their composition and structure.

Three major hypotheses will be tested:

- 1 - mechanism of formation: PY precipitating at ambient conditions from aqueous solution containing REE or U incorporates preferentially these metals into the structure lowering significantly their concentration in the solution. Thanks to a very high removal efficiency, PY acts as a filter with respect to REE and U. There is no data on the mechanism and limitations of formation of REE-rich or U-rich lead apatites upon precipitation from aqueous solutions at ambient conditions. This will also shed light on the explanation of the relationship between REE-rich pyromorphites and concentrations of REE in natural waters indicated by literature. The removal efficiency is also important in terms of future potential applications for removal of REE or U from aqueous solutions.
- 2 - structural position: despite the similarities between Ca-apatites and pyromorphite, substitution mechanism and structural position of REE and U in PY precipitated from low-temperature aqueous solutions is different than this known from igneous and hydrothermal Ca-apatites. Structural limitations of multi-element substitution at low temperature are unknown for both, lead and calcium systems. This is particularly important in terms of U and future applications of Pb-apatites in remediation of radioactive waste.
- 3 - the extent of substitution: PY can incorporate more (and less fractionated) REE or U than Ca-apatite due to the larger unit cell. Although these minerals are present only as accessory minerals in many low-temperature systems, the significance of this process may be great in terms of the understanding of the release of REE to natural solutions, recovery of REE during phosphate fertilizer production or development of the technologies for the storage of actinides extracted from nuclear waste.

Scientists need to intensify research into REE phenomena, their recovery and materials, to keep pace with the development and needs of modern technologies. This proposal identifies an important and wide area of ignorance and proposes basic research to reduce it. The international team that undertakes this task consists of the best experts in the field of experimental mineralogy as well as in structural, chemical and mineralogical studies of rare earths and apatites, and Pb-apatites in particular. This guarantees the highest quality results and the dissemination of results in a wide and diverse scientific environment in the world. The results will extend our knowledge of natural environments (mineral-water interactions) and of material science and geofunctional materials which can be used in industrial technologies. The strength of current application stems from extreme novelty of this research and from the arising possibilities for future applications.