

Low temperature transformation of monazite (Ce,U,Th)PO₄ into pyromorphite Pb₅(PO₄)₃Cl – basic study for future technologies

Mineral monazite CePO₄ and monazite-based ceramics are recommended in radioactive waste technologies because they are resistant, durable and have very low solubility. During dissolution in aqueous solutions, the monazite materials become coated with a layer of secondary phosphates, passivating the surface and slowing down the dissolution. This project will test the hypothesis that in the presence of Pb²⁺ and Cl⁻ ions the dissolution of natural monazite (Ce,U,Th)PO₄ proceeds differently than in pure aqueous solutions: it is accompanied by crystallization of pyromorphite Pb₅(PO₄)₃Cl which accelerates the process of monazite decomposition and may reduce its properties as a material for use in repositories of radioactive waste. Lead is commonly used in all technologies related to radioactive materials so the existence of solutions containing Pb²⁺ ions is very likely in association with radioactive waste and related installations.

Although the solubility of monazite is low (solubility constant $K_{sp} = 10^{-28}$ at 25 °C), pyromorphite has an even lower solubility (solubility constant $K_{sp} = 10^{-84}$) making its formation preferable in the environment. Low monazite solubility is accompanied by low dissolution kinetics due to surface passivation. A thin layer of phosphate-based products of incongruent dissolution is formed on the surface which limits the access of fresh solution and slows down the reaction. However, the solubilities of all substances forming the passive coating are much higher than those of pyromorphite which, in the case of competing processes, also favors the precipitation of pyromorphite.

Thus, there are both thermodynamic premises and literature concerning the formation of transition, metastable phosphates indicating, that in the presence of Pb²⁺ and Cl⁻ ions the precipitation of pyromorphite Pb₅(PO₄)₃Cl as the phase with the lowest solubility in the system is possible and probable: dissolved monazite would be a source of phosphate ions and the process would be controlled by the availability of Pb²⁺ and Cl⁻ ions. No one has explored this possibility before. This should be a competitive process for the formation of other phosphates. Pyromorphite will act as a sink for the PO₄³⁻ ions released during dissolution of monazite. It may disturb the equilibrium and result in further dissolution of monazite by le Chatelier's principle. Since the only source of PO₄³⁻ is dissolving monazite, the reaction will theoretically continue until the components available for precipitation of pyromorphite are exhausted. The identification of the structures of precipitated phases, the formation of layers, coatings, pseudomorphs and other forms which can hinder the progress will also be the aim of research.

The research is proposed to be conducted in three stages:

- 1) Dissolution of monazite in the presence of Pb²⁺ and Cl⁻ in solution: macroscopic description of the effect of experimental conditions on the course of the reaction and products of transformation (solids and solutions). Powdered monazite will be dissolved in solutions of different pH and composition, containing Pb²⁺ and Cl⁻ ions (the control experiment in the absence of Pb and Cl). Solids and solutions will be analyzed before and after the experiment. This part of research will be run at the laboratories of AGH in Kraków.
- 2) Mechanisms of monazite replacement by pyromorphite. The subject will be the surface of the reacting monazite, the phases formed on the surface and the mineral-water interface. Optically clear, single crystals of natural monazite will be used as starting material for the experiments. The ex-situ experiments and the in-situ experiments (using fluid-cell Atomic Force Microscopy) will be run to study the structure and composition of secondary phases as well as elementary mechanisms of monazite incongruent dissolution and reactions with solutions by analyzing the surface with subatomic resolution in real time directly in solution. This part of research will be run at the laboratories of AGH in Kraków.
- 3) Synthesis of pyromorphite analog in the presence of Ce and trace U and Th, similar to those resulting from the experiments described above. The crystalline structure and spectroscopic manifestations of the presence of these ions will be analyzed so that in the future it will be possible to unambiguously identify and explain the presence of such substitutions in lead apatites. So far, the presence of such ions in the pyromorphite structure has never been studied. This part of the project will be carried out as part of the internship (co-financed by NAWA) in the University of Notre Dame, Indiana, USA at the Energy Frontier Research Center, Materials Science of Actinides under the joint supervision of the PI and Dr. Peter Burns, the director of the Center.