

## Abstract

This study investigates alteration processes of xenotime, monazite and zircon in microscale down to nanoscale. The investigations include evaluation of the natural cases of alteration of zircon, monazite and xenotime, and monazite and xenotime from products of laboratory experiments conducted under P-T conditions of 200 MPa / 350 °C, 400 MPa / 450 °C, 600 MPa / 550 °C, 800 MPa / 650 °C and 1000 MPa / 750 °C. The main goal of this study is focused on evaluation of textural, structural and compositional characteristics using a variety of analytical methods on unaltered and altered domains to improve our understanding of alteration processes that affect zircon, monazite and xenotime.

The first part of this study focuses on an altered zircon-xenotime intergrowth from pegmatite from Piława Górna (Góry Sowie Block SW Poland). Investigations were conducted at microscale and submicron-scale with transmission electron microscopy (TEM) and laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). The strongly altered zircon and xenotime demonstrate distinct domains related to fluid-induced coupled dissolution-precipitation processes that resulted in development of micro- to nanoporosity in both zircon and xenotime, and diffusion-reaction processes in the metamict zircon core. Secondary inclusions include fluorapatite, unknown layered Fe-silicates, fibrous Fe-oxides, solid solutions of coffinite-thorite and uraninite-thorianite, uraninite and secondary U-rich zircon. The fluid supplied zircon and xenotime with Ca and Fe, while mobilizing U, Th and Pb.

The second part of this study focuses on Raman microspectroscopic study of monazite and xenotime from the products of laboratory experiments using 488 nm, 532 nm, 633 nm and 780 nm excitation lasers in combination with compositional measurements using electron probe microanalysis (EPMA) and LA-ICPMS. Additional Raman microspectroscopy was conducted on altered monazite from Ankazobe (Madagascar), altered xenotime from pegmatite from Piława Górna, and synthetic REE-phosphates ( $\text{LaPO}_4$ - $\text{LuPO}_4$  and  $\text{YPO}_4$ ). Monazite spectra (532 nm) display shifts of the  $\nu_1(\text{PO}_4)$  symmetric stretching band from 969–981  $\text{cm}^{-1}$  to 962–965  $\text{cm}^{-1}$ , formation of a new band at ca. 861–869  $\text{cm}^{-1}$  and broad fluorescence peaks at ca. 2028  $\text{cm}^{-1}$  and ca. 3287  $\text{cm}^{-1}$ . Raman spectra of xenotime from experimental products display characteristic features in the form of fluorescence effects in the range of 200–700  $\text{cm}^{-1}$  caused by  $\text{Ho}^{3+}$  ( $^5\text{S}_2 \rightarrow ^5\text{I}_8$ ) and  $\text{Er}^{3+}$  ( $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ ) electronic transitions. Raman spectra of Y-rich fluorcalciobriholite display characteristic changes of fluorescence effects at the range of 1500–3000  $\text{cm}^{-1}$  with a significant increase in the fluorescence peak at ca. 2600  $\text{cm}^{-1}$  caused by  $\text{Sm}^{3+}$  ( $^5\text{D}_0 \rightarrow ^7\text{F}_3$ ), and is accompanied by a new band at 974  $\text{cm}^{-1}$  (488 nm) and 964  $\text{cm}^{-1}$  (633 nm). Fluorescence effects remain a difficult artefact in Raman microspectroscopy of xenotime, whereas, at the same time they enable differentiation of xenotime and Y-rich fluorcalciobriholite in hyperspectral mapping.

TEM investigation of microscale to submicron-scale alterations of xenotime and zircon from pegmatite from Piława Górna are in good agreement with its geochemical characteristics and emphasize the importance to identify nano-inclusions and their abundances which otherwise remain undetected

with microscopic methods. The spectral characteristics of unaltered and altered monazite and xenotime enable identification of structural changes, presence of secondary phases and expand the Raman database. Results of both analytical approaches, TEM nanoscale evaluation and application of Raman microspectroscopy provide complementary information to petrochronological interpretation and timing of various processes that affected the rock during its formation and when transformed or reworked during tectonometamorphic events.