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Report on the PhD work of Fabian Tramm presents a study on "Micro- to nanoscale constraints on fluid-induced alteration processes of zircon, monazite and xenotime – experiments and nature" supervised by prof. Bartosz Budzyń, PhD.

I have been very honoured to be appointed by the Scientific Council of Geological Sciences of the Polish Academy of Sciences as a reviewer of the doctoral dissertation of Fabian Tramm. This work was made under the supervision of Bartosz Budzyń, PhD, who is an international expert on the stability of accessory minerals and their behavior during alteration, with implications for geochronology. I had pleasure to evaluate this doctoral dissertation: it is a high-quality work that will significantly contribute to improving our knowledge on the alteration mechanisms of zircon, monazite and xenotime.

Introduction and structure of the manuscript

The manuscript of 178 pages (including references but with separated Annexes) is subdivided in 6 chapters. The aims of the work are well presented and show the structuration of the manuscript with the results obtained through this work into two main chapters (3 and 4). It is an extremely clear, well-written, and well-structured manuscript. The literature references are up to dated and well presented in the last chapter 6.

The introduction clearly defines the aims and structuration of the doctoral dissertation. The accessory minerals investigated in this study, namely zircon/xenotime/monazite, are of prime importance in Earth Sciences because these minerals are main hosts for U and Th, and thus main U-Th-Pb geochronometers for Earth History reconstructions. Understanding their alteration is thus crucial to evaluate the possibility of age resetting and possible disturbances in the isotopic decay systems. This requires very detailed mineralogical, chemical, structural investigations up to micro- to nanoscale as presented in the introduction.

The second chapter makes a brief summary of previous works on zircon, monazite and xenotime. It presents a state of the art on the literature on these accessory minerals, concerning their occurrences, their natural and experimental stability and their alteration mechanisms. The reference list is complete and exhaustive: it presents the precursor studies as much as the most recent literature. While the behaviour of zircon and monazite during alteration has been already investigated in numerous studies that are well cited in this chapter 2, it shows well that this is not the case for xenotime, for which much less is known. Similarly, there is much less work on spectroscopic measurement for this latter mineral. This is an important point for this PhD that contributes to refine our understanding on this specific mineral.

Results and Implications

The third chapter presents a natural case-study of alteration of zircon-xenotime using high-resolutions in-situ techniques to obtain compositional data (LA-ICP-MS) and nanostructural observations and characterizations (TEM). The investigated material is pretty exceptional. It is made of a plurimillimetric intergrowth of xenotime/zircon in a pegmatite from Pilawa Gorna (Gorie, Sowie Block, SW Poland). This assemblage was originally formed at 2.09 Ga and taken as a restite in a pegmatite dated around 370 Ma. The new in situ geochemical data indicate that U contents are very high for zircon. Combined with the old original age, favour radiation damage that could probably explained the complexity of the observed nanostructures. Indeed, the novel TEM observations are outstanding: they show the distribution at nanoscale of the alteration and fluid transfer through the nanopores and the nanoinclusions typologies. These new data reveal a contrasted alteration mechanism within a single grain from diffusion driven in the core to dissolution-precipitation driven in the rim. In xenotime, the mechanism is attributed to dissolution-precipitation. The inclusions reveal

some Pb mobility (galena inclusion) and preferential U-Th-secondary mineral precipitation that may impact the geochronological dataset. It proves the importance of the nanoscale observations for better understanding the age significance. This nanoscale study is really impressive and was already published in Tramm et al., (2021). The figures are of high-quality, but they may have been more abundant to illustrate this chapter. Especially, it may have been useful to profit of this manuscript to show more material on the samples that were investigated (Additionnal field, macro,… images).

The fourth chapter is a very careful and complete evaluation of the potential of RAMAN spectroscopy to characterize monazite and xenotime. This study was thoroughly conducted on natural and experimental samples showing different degree of alteration. Furthermore, the effect of the alteration temperature could be evaluated through the characterization of experimental samples altered under different conditions. This is very important because temperature can have two combined effects on the mineral alteration reactions. It can both favour alteration and solid state (annealing) of initial radiation damages caused by U and Th radioactive decay. Finally, mapping obtained through RAMAN and EPMA on experimentally altered material was used. These new results provide an excellent database for understanding their RAMAN signature. They show that the monazite spectra are much more complex than those of xenotime, and this makes difficult to correlate spectroscopic measurements with the complex REE, Th, U and Pb composition of monazite. On the other side the broadness marked by the FMWH of the main peak vibration of monazite seems very interesting to characterize the crystallinity and possibly to detect the different crystallisation domains. I am sure that these data are important for the mineralogy community and that the results deserve publication.

The Conclusions (3 pages/chapter 5) make a clear summary of the main results obtained through the study and their implications. From my opinion, the most important conclusions can be summarized as follows with some questions that could be considered the day of the defense.

- Understanding the zircon/xenotime alteration mechanisms with concomitant dual processes exerting in a single grain, with different inclusion typologies and element mass transfer. I was questioning what are the reasons behind the coexistence of the two mechanisms? Is it only a question of the distance of the environment as proposed on Figure 18?
- Tracking the fluid composition responsible of natural alteration through the characterization of inclusions in altered U-Th rich accessory minerals. How do you think that primary and secondary inclusions can

be distinguished.

- Micro to nanoscale evaluation of the impact of accessory mineral alteration on geochronological datasets, especially due to possible U-Th-Pb disturbances depending on their mobility during rock/fluid interactions. I was surprised that the geochronological dataset of the xenotime was so discordant. If dissolution/precipitation occurs, what are the reasons behind the incomplete resetting?
- New database for RAMAN applied to actinide and REE-rich accessory minerals. It would be very interesting to discuss in detail the complement that bring this method in comparison to other in-situ geochemical data that are based on element and isotopic compositions

Concluding remarks for the evaluation

In conclusion, Mr. Fabian Tramm, MSc, presents a doctoral dissertation that attests of his ability to independently conduct a scientific research work. The scientific methods were thoroughly applied to obtain results that brings some new light on the alteration of zircon, xenotime and monazite. This work will certainly have important implications for the Earth Sciences community, especially in the fields of geochronology and petrology of accessory minerals. The reviewed PhD thesis of Fabian Tramm meets all the legal requirements for PhD dissertations in light of the provisions of the Law of July 20, 2018. - Law on higher education and science (Journal of Laws of 2022, item 574, as amended). **Thus, I apply for admission of Mr. Fabian Tramm to further stages of the doctoral program of the Institute of Geological Sciences of the Polish Academy of Sciences.**

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