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Dissertation review

Fabian Tramm: Micro-to nanoscale constraints on fluid-induced alteration processes of zircon, monazite and xenotime – experiments and nature.

Dissertation thesis according to the assignment presents the results of research on stability of zircon, monazite and xenotime, which as the principal accessory phases in felsic magmatic rocks are main carriers of incompatible elements in natural magmatic systems controlling their behaviour. The dissertation represents a work of mineralogical basic research and consists of two parts. The first one is a detailed structural and compositional investigation performed on 2 mm large grain of zircon/ xenotime intergrowth which was extracted from pegmatite in Piława Górna. The second part is focused on the systematic Raman microscopic measurement of variable monazite and xenotime compositions but mainly on large set of experimental research products carried out under different pT conditions. Beside the analysis of experimental runs, Raman microspectrometry was applied also on naturally altered monazite from Madagascar and xenotime from Pilawa Górna. The Raman measurement was completed by compositional analyses by using electron microprobe and LA ICP MS technique rendering the research very innovative. The research was performed through international collaboration when some data was gathered in Prague (Czech Republic) and in GFZ Potsdam and Ulm (Germany). The first part of results were already published by author in the reputable journal Lithos demonstrating the high quality of performed research.

Structure of the dissertation, originality and used methods

The entire manuscript is written in English on 176 pages, including reference list on 27 pages. The author used up to date analytical methods and measurement conditions were properly introduced and explained, primary analytical data are shown in added Tables recorded on CD. Tables which belong to the first dissertation block present zircon, xenotime and apatite trace elements compositions, eight Raman spectroscopical Tables complete the second part and the obtained data

in such way are prepared for a possible further re-use. In general, the structure of the doctoral dissertation is logical, figures and drawings are well designed, the reference list is adequate to the topic. In overall, my expectations for the quality of the dissertation thesis, accomplished under the supervision of Dr. Bartek Budzyń, have certainly been fulfilled.

The both parts of the dissertation have been well introduced by a survey of existing modern literature in four subchapters devoted to stability of monazite, xenotime and zircon and the utilisation of Raman microspectrometry. The first part is a detail description of natural zircon and xenotime paragenesis by high-tech equipment recently utilised in very modern mineralogical research, specifically impressive are the analyses performed on 11 only 20 x 2 μm large foils separated by the focus ion beam technique. The zircon/xenotime intergrowth analyses obtained by high-resolution LA ICP-MS device, located at the Institute of Geology of the Czech Academy of Sciences (Prague, Czech Republic), revealed the details of textural and compositional character of all investigated minerals and compositional inhomogeneities indicated by BSE images. Transmitted electron microscope (TEM) observations on liberated foils from the grains were performed at the German Research Centre of Geoscience (GeoForschungsZentrum GFZ, Potsdam, Germany), TEM was equipped with an Electron dispersive X-ray analyser (EDAX) and a Gatan electron energy-loss spectrometer (EELS) for the investigation of the composition in nanoscale and results are unique.

In the first part the research presents the results of fluid mediated regime indicted by Fe impurities, which intensively affected investigated Pilawa zircon and xenotime natural paragenesis. The discovery of diffusive changes in zircon core or its micro and nanoinclusions, is an excellent finding for general petrological and geochronological outreach. Especially surprising was the finding of newly formed tiny zircon phase formed inside of a large zircon grain. It means the core of zircon in the Phanerozoic age was affected by diffusion, but the rim with a lot of nanoporous and microporous areas represents a site where dissolution/reprecipitation process was in progress. I found the summary of the first part, showing elemental mobility in the investigated mineral zircon/xenotime microsystem, to be a good guideline for worldwide application in the fluid mediated felsic magmatic systems. Interesting was also to see unclear confrontation of zircon compositions in diagrams for identification of magmatic stage.

The second part of the dissertation offers systematic Raman study of altered xenotime from Pilawa Górna, but here the main focus was on altered natural and synthetic monazite and xenotime prepared for experimental runs performed in piston-cylinder apparatus located at GFZ Potsdam at various 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. Raman measurement was done partly in Ulm (Germany), but mainly at the Jagellonian university at room temperature. This research showed that the best way how to collect

Raman data is by using the 633 nm laser, which provide the most fluorescence free spectra. The description of measured monazite and xenotime was perfectly documented by BSE images with points where the spectres were obtained, the compositional analyses done by EMPA and the location where the LA-ICP MS analytics were performed. The selected position of Raman microstructure was shown as well. All monazite composition are presented in Tables B3 and B4, xenotime in Table B6. It is fine to see that the calculated FWHH values based on compositional EPMA data fits well with the measured values. Hyperspectral mapping of xenotime demonstrated the potential how to identify secondary phases under surface of the mount mineral. The Raman spectra combined with the compositional data are used to identify the alteration mechanism such as thermal annealing, or recrystallization. The research thesis showed that the hyperspectral maps are more effective in the case of monazite but not very useful for xenotime. Author tried effectively interpret all data.

Topicality of dissertation

The present dissertation solves the problem of stability of accessory minerals, which are commonly used in the petrological interpretation and in the metallogenetic applications. The mineral stability of rare earth minerals is recently intensively studied also for their potential as critical metals for modern smart technologies. The performed research clearly shows that zircons from evolved magmatic system is problematic for dating. All information lead to better understanding of stability of principal mineral carriers of REEs and thus the dissertation topic is really very actual.

Critical remarks and queries

The geological background is not presented deeply enough to understand how the host rock, where zircon/xenotime intergrowth was separated from, looks like. It is a very important issue for wider application of results in genetic mineralogy. Petrographic description is not sufficient, and pegmatite zoning in Pilawa Górna should have been presented as well. The location map is very general, the position of sampled site is hardly visible on the map

Some clarification is needed as following:

1. Which pegmatite zone was the grain of zircon/xenotime intergrowth taken from? Is the zircon/xenotime intergrowth from the graphic zone or from the wall zone?
2. Problem of diffusion? What phase is the yellow part surrounded zircon and xenotime on Fig. 3b from? When this diffusive effect occurred? During Permian stage?
3. Why was the Raman investigation performed only on xenotime and not also on associated zircon – it could be interesting to see the spectra from different patches.

4. Chapter 4.3.1 presents, among others, that altered domains in the Burnet monazite is depleted in Th, U and Pb but data in the Table B3 not fully supporting this view. Can you discuss the statement?
5. Should the mean indicator for the altered site be really depletion in U and Th? Fig. 19 documents the Raman, EMPA and LA-ICP MS spots, but EMPA unaltered points 9 and close altered 4 show similar compositions in Th.
6. Large Ankazobe monazite is altered on the entire rim or alteration only local? The altered rim cannot be just intergrowth with micas and xenotime from the host rock independently accreted to monazite?
7. What kind of recommendation can be drawn from your research? BSE and EMPA or combination BSE and Raman is more sufficient to indicate an alteration?

Concluding statement

This doctoral dissertation shows how the fluid-induced alteration changes the composition and the structure of the minerals, and well demonstrates the importance of sub-micron investigation. The application is in petrology because affected monazite, xenotime and zircon by fluids can provide potential misinterpretation in geochronology. Significant band narrowing in Raman spectra in the combination with compositional data indicates the presence of recrystallized domains by process of dissolution-reprecipitation controlled by environmental fluids forming also porous fabric. On the other hand, thermal fluid activity triggers in minerals only diffusive alteration and structure annealing. The dissertation is well presented theoretically and experimentally and demonstrates the ability of the author to independently solve complicated fundamental scientific tasks. A lot of analytical data became the basis of high-quality publication but there is also a potential for further outcome in the data.

The dissertation is of a good quality and thus can become the basis for the PhD defence. I recommend Fabian Tramm to be awarded the title of philosphiae doctor.

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RNDr. Igor Broska, DrSc.