TUBAF
Die Ressourcenuniversität.
Seit 1765.

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Review

of the member of the dissertation council for the dissertation of ***Klimova Ekaterina Vladimirovna*** *on the topic: "Drainage solution geochemistry in relation with formation of Precambrian weathering crusts of the Fennoscandian Shield", submitted for the degree of candidate/doctor of geological and mineralogical sciences in scientific speciality 1.6.4 Mineralogy, crystallography. Geochemistry, geochemical methods of prospecting for deposits.*

The aim of this scientific work is to better understand the conditions that led to the formation of widespread Precambrian weathering crusts on the Fennoscandian Shield. In **Chapter 1** (Structure, composition, geochemical features of Precambrian weathering crusts in Karelia) the author gives concise definitions for the most important terms (e.g. eluvial deposits, hypergene drainage solutions), followed by the description of most important weathering features and typical profiles of Precambrian weathering crusts (along with major physical, mineralogical and chemical changes) of the Fennoscandian Shield. The Chapter is very well written and thus provides a good introduction to the topic. In **Chapter 2** (Geology of the area of work) a general introduction to the geology of the Eastern part of the Fennoscandian Shield is given, followed by a more detailed description of the two study areas (Yanisjärvi structure, Lekhta structure). Ekaterina Vladimirovna Klimova took part in these field excursions and the development of new detailed maps (Figs. 4, 13). She studied rocks from these outcrops and gives detailed descriptions of their structure and mineralogy in this chapter. In the following **Chapter 3** (Features of chemical composition of the Paleoproterozoic weathering crust in Karelia) Ekaterina Vladimirovna Klimova provides results of chemical changes from these two working areas that occurred in the weathering profiles. This chapter is very short (2 pages) and does not go into detail but describes only the most dominant changes.

One of the specified goals of this study was the development of an experimental approach to better understand (i) leaching processes and the accompanied enrichment of elements in drainage solutions and (ii) the interaction of drainage solution with authigenic clay components and to study the associated chemical changes in the drainage solutions. **Chapter 4** (Material and experimental technique) gives a detailed description of both types of experiments and the used

materials together with their chemical characterization. In total, more than 50 experiments were performed with different durations, pH-values, and oxygen concentrations (oxygen atmosphere compared to argon atmosphere). To obtain non-metamorphosed analogues of the clay zone of weathering crusts (all Precambrian outcrops are metamorphosed and clay minerals transformed mostly to muscovite and biotite), Ekaterina Vladimirovna Klimova also studied clayey deposits from various caves by XRF and geochemistry, and separated the clay fraction from these samples. Sample locations, samples, and XRF and chemical results are given in **Chapter 5** (Reconstruction of the mineral composition of the clay zone in the Paleoproterozoic weathering crust of Karelia). **Chapter 6** (Geochemistry of drainage solutions) is the longest chapter (26 pages) and first gives a detailed description of the results of various leaching experiments (Section 6.1). The experiments resulted in contrasting and very interesting chemical behaviour for different conditions (mainly depending on pH and the presence or absence of oxygen in the atmosphere). These results form the base for the first thesis statement that leaching could have occurred only under oxidising environments and that acid solutions are able to mobilise many elements from the weathered rocks. In the second part (Section 6.2) the results of interaction of water with clay sediments (the second type of experiments) are compared with results from leaching experiments. The contents of Light Rare Earth Elements (LREE) are about 1000 times lower compared to leaching experiments under oxidising environments with acid solutions. This fact is formulated in the second thesis statement and interpreted as the results of sorption of these elements to the clay fraction. Another important observation is that all solutions changed to alkaline conditions during interaction with the clay fraction. Finally, it was shown by the experiments that the ratio K/Na can be ≥ 1 only during leaching at acid conditions but not during interaction of drainage solutions with clay material. This is defined as the third scientific statement of the thesis.

In summary, a lot of experiments were performed by Ekaterina Vladimirovna Klimova that really led to a better understanding of the conditions necessary for formations of Precambrian weathering crusts. Therefore, this work provides new results (especially obtained by experiments) and tried to outline the most important parameters necessary for the formation of weathering crusts and geochemical changes in drainage solution during two stages: (i) leaching, and (ii) interaction with newly formed authigenic clay minerals. It develops and discusses innovative ideas (oxygen content in atmosphere during Precambrian, the role of K/Na for favourable environmental factors for the emergence of life in continental settings). However, in few places I wished a more detailed explanation or discussion (for instance when and how the pH changed during interaction with

authigenic material). Here I formulate a few questions which I look forward to hearing the candidate answer.

Question 1: You mentioned and discussed the negative Ce anomaly in the drainage solutions in your leaching experiments (acidic oxidising conditions) for short durations (< 1 hour). How do you explain the absence of the Ce anomaly for longer experiments? Does the absence of the Ce anomaly for longer experiments mean that dissolved oxygen was absent and could be consumed by some reactions? If yes, what reactions do you suggest?

Question 2: In Figure 37 I cannot see a trend with longer duration of the experiments. How do you explain the absence of such a trend? Can you estimate how large is the error of each individual measurement/ for each experimental run?

Question 3: You mention and underline the very low REE contents (especially LREE) in your solutions during interaction with the clay material. Can you please discuss the (L)REE contents of the used clay material in connection with the (L)REE contents of your solutions? Can you please also relate the (L)REE contents of the used solutions (your Table 4.4)?

Based on the arguments given above I have no doubt that the dissertation of Ekaterina Vladimirovna Klimova "Drainage solution geochemistry in relation with formation of Precambrian weathering crusts of the Fennoscandian Shield" meets the requirements of scientific speciality 1.6.4 Mineralogy, crystallography. Geochemistry, geochemical methods of prospecting for deposits.

The dissertation is a scientific qualification work that resolves an important scientific problem (formation of Precambrian weathering crust and associated geochemical changes) and provides innovative ideas.

No violations of paragraphs 9 and 11 of the Order No.11181/1 as of November 19, 2021 "On the Procedure for Awarding Academic Degrees at St. Petersburg State University" have been detected.

The dissertation meets the criteria of dissertations for the academic degree of candidate of sciences, established by the specified Order. The dissertation is recommended for the defense at St. Petersburg State University.

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Herewith, the personal signature of ..Tichomirowa, M.... is certified.

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