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PHD THESIS SUMMARY

Geochemistry and mineralogy of river bed sediments from the basins of the Ditrău and Jolotca valleys (Ditrău Massif)

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Abstract

Ditrău Alkaline Massif is one of the few syenitic Massifs in Europe subjected to mining exploration in the past, located in the Eastern Carpathians, Romania. The heterogenous petrography includes acid to ultrabasic rocks such as syenites, hornblendites, and diorites, making it the defining feature of the Massif. In this study, I analyzed the river bed sediments of two rivers, Ditrău and Jolotca, draining the Ditrău Alkaline Massif to determine their geochemical composition, with particular interest in Rare Earth Elements. The analysis was carried out with various analytical methods, including Inductive Coupled Plasma Mass Spectrometry, powder X-ray diffractometry, and electronic microscopy for mineralogical analysis to determine the presence of heavy minerals and quantify the concentration of Rare Earth Elements in the river sediment samples. The results indicate the existence of heavy minerals and Rare Earth Elements in bearing minerals such as Monazite and Epidote. High concentration values of Light Rare Earth Elements are identified, with values more than double compared to the Upper Continental Crust in some cases, of which stands out Cerium with 175.47 $mg \cdot kg^{-1}$ and Lanthanum with 108.32 $mg \cdot kg^{-1}$. Most samples share three main minerals: Quartz, K Feldspar, and Albite, while Diopside is only present in the Jolotca sediment samples, and Plagioclase exists in Ditrău samples. Moreover, many identified trace elements, such as Niobium, Tantalum, and Zirconium, indicate high enrichments, with samples' mean value of 265.62 $mg \cdot kg^{-1}$ for Zirconium and 200.24 $mg \cdot kg^{-1}$ for Niobium. The sum of Rare Earth Elements identified in the analyzed river sediments is 385.01 $mg \cdot kg^{-1}$ for Ditrău samples and 368.72 $mg \cdot kg^{-1}$ for Jolotca, with Cerium being the most significant element. The La/Th and Hf distinction plots suggest a mixed felsic/basic source for the Ditrău area and an acidic source for the Jolotca area.

Naturally occurring ^{238}U, ^{232}Th and ^{40}K radionuclides within river bed sediments of Jolotca and Ditrău rivers from Ditrău Alkaline Massif (DAM) and their environmental risk and spatial distribution have been analyzed. The DAM metamorphic formations have been the subject of multiple studies due to their structure and high variety of mineral species. This led to the execution of many mining operations. River bed sediment samples have been collected from two of the main drainage basins of DAM, Ditrău and Jolotca rivers. The samples were analyzed using gamma-ray spectrometry in order to determine the concentration of the naturally occurring radionuclides and the risk parameters such as RLI (Representative level index), AGDE (Annual gonadal dose equivalent), Hex (External hazard index), Hin (Internal

hazard index) and DR (absorbed gamma dose rates in air). 238U, 232Th and 40K show values higher than the Upper Continental Crust (UCC) and other studies from around the world. DR, AGDE and RLI are higher than the global average and the safe limits. These values are a consequence of the geological context which determined the presence of heavy minerals and Th and U bearing minerals.

This study aims to analyze the geochemistry of the river sediments focusing on the REE concentrations but also including the analysis of heavy minerals and trace elements. Naturally, the Massif is defined by significant REE concentrations, however, the influence of anthropic activities in the area were never really accounted for. Hence, the geochemical analysis of the riverbed sediments in the Ditrău and Jolotca rivers will provide significant information about the human impact on the environment. We expect higher concentrations of REE along the Jolotca River, which drains through areas subjected to mining activities in the past. We will also quantify the concentrations of REE in the river sediments and relate them to global standards such as the UCC to evaluate the possible enrichments of certain elements. Moreover, the analysis of the geochemical and mineralogical properties of the riverbed sediments will provide a better understanding of the geological source of the sediments within the DAM.

Also, a main objective of this study is the determination of the spatial distribution of the naturally occurring radionuclides ^{238}U, ^{232}Th and ^{40}K in the river-bed sediments of the Jolotca and Ditrău rivers from the Ditrău Alkaline Massif (DAM) and their associated radiological risk assessment.

In this work, I used the river bed sediments sampled from the Jolotca and Ditrău rivers to determine their geochemical composition, explicitly focusing on REE, and get more significant data about the geochemistry of the Massif. I identified and analyzed the presence of the REE and the content of heavy minerals and trace elements. In the riverbed sediments from DAM, the whole range of REE, from La to Lu, was identified in the bearing minerals of the area, such as Monazite and Epidote. The analysis revealed that LREE, particularly Cerium (Ce) and Lanthanum (La), are found in concentrations exceeding the UCC's. For instance, Cerium concentrations have values of 175.47 $mg \cdot kg^{-1}$ in the Ditrău samples, while Lanthanum reached 108.32 $mg \cdot kg^{-1}$, both of which are over twice the UCC reference values. Regarding mineralogical composition, Quartz, K Feldspar, and Albite are found across the river sediments, though Diopside appeared exclusively in Jolotca sediments, and Plagioclase was unique to Ditrău. The presence of trace elements like Zirconium, Niobium, and Tantalum also stood out, with the sediments showing high concentrations of Zirconium at 265.62 $mg \cdot kg^{-1}$ and

Niobium at 200.24 $mg \cdot kg^{-1}$. These enrichments indicate a complex geochemical background influenced by both natural geological processes and anthropogenic activities.

The EF values in the Jolotca sediments are higher than those in Ditrău, particularly in the range of 20–40 of the "very high" class for Jolotca, compared to the "significant" class range of 5–20, which are in Ditrău samples. This disparity likely reflects the influence of historical mining activities near the Jolotca River, which might have contributed to the higher concentrations of REE. The Ce anomaly and the Ndn/Ybn ratio that we used as indicators of lithogenic supplies indicate values well above the threshold for significant lithogenic input for both rivers, further underscoring the presence of fresh geological material in the sediment supply. Also, the La/Th and Hf distinction plots provide significant insights into the geological origin of the sediments. These plots indicate a mixed felsic/basic source for the Ditrău area, while the riverbed sediments from the Jolotca River point to an acidic source.

This study confirms the abundance of REE in the Ditrău and Jolotca rivers, which derive from both natural lithogenic sources, but also highlights the impact of the anthropogenic activities, particularly in areas like Jolotca, where past mining operations have left a significant imprint on the local environment. Also, the differentiation in sediment origin highly contributes to the understanding of the geological history of the massif and its geochemical composition. This geochemical analysis enriches our understanding of the Ditrău Alkaline Massif and provides crucial data on the environmental impacts of human activity in the region, which should further be evaluated and monitored.

All naturally occurring radionuclides ^{238}U, ^{232}Th and ^{40}K show values well above the continental crust values and higher than those obtained in other studies. For ^{238}U and ^{232}Th the higher values are due to the minerals like xenotime, epidote, calcium and phosphate minerals bearing REE found in the surveyed area. On the other hand, the high ^{40}K values are due to the alkaline, K-feldspar-rich nature of the massif.

While the Absorbed gamma dose rate (DR), Annual gonadal dose equivalent (AGDE) and Representative level index (RLI) show values well above the world average and acceptable limits, this can be attributed to the geological context, the presence of heavy minerals and the fact that in the studied area U and Th bearing minerals have been previously described.

This thesis is structured in 5 main chapters and are ordered as it follows:

Chapter 1 “Natural setting of the study area” tackles both the location of the area, geomorphological aspects, but mostly is focused on the geological setting and its history. Chapter 2 “Sampling and analytical methods” describes the field trip and survey of the study

area, and explains all the analytical methods that wore used for this thesis, especially for the mass spectrometry analysis.

Chapter 3 “Results” lists all the findings of this thesis, from the minerals identified in the samples, the trace elements analyzed and notable the Rare Earth Elements and their concentrations in each sample.

Chapter 4 “Discussions” takes the results of this thesis and compares them to the international standards, such as the Upper Continental Crust and other studies from around the world, in order to asses if we have an enrichment in different elements or a depletion.

Chapter 5 “Conclusions” states the most important findings in our study, the originality element of it, and the necessity of this study and the main factors that led to enrichment or pollution in different elements.