GEOCHEMICAL DISTRIBUTION OF LANTHANIDES, URANIUM AND THORIUM IN SOILS OF THE DITRĂU MASSIF

PhD THESIS

ABSTRACT

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The Ditrău Alkaline Massif, unique by its mineralogical and petrographical variety, is considered to represent an intrusive body with an internal zonal structure emplaced in metamorphic basement rocks belonging to the Tulgheș Group, in the thrust sheet of the crystalline-Mesozoic units of the Eastern Carpathians. The existing geological data show that the large variety of alkaline rocks which occur in the Ditrău Massif (hornblendite, diorite, syenite, nepheline syenite, monzonite, monzodiorite, aplite, granitoids) is fairly rich in rare earth elements (REEs) and natural radioelements (U and Th). In all these rocks, the REEs, U and Th are constituents of the accessory minerals such as allanite, chevkinite, cerite, monazite, fluorapatite, apatite, xenotime, bastnäsite, parisite, synchysite, hydroxylbastnäsite, thorite, thorogummite, pyrochlore, columbite, fergusonite, euxenite, aeschynite, zircon, fluorine, titanite, garnet. A small fraction of REEs, U and Th is present in the main silicate phases as isomorphic substituents of the major cations, such as in: microcline, albite, oligoclase, augite, nepheline, muscovite, biotite, cancrinite, hornblende.

The main objective of the PhD thesis is derived from this feature of the massif and consists in assessing the geochemical levels of lanthanides (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, Y) and natural radioactive elements (U, Th) in soils developed on alkaline rocks and contact rocks, on an area of approximately 625Km^2 covering the Ditrău Alkaline Massif. For this purpose, geochemical distribution maps (mono and multi-element) were built for soils, consistently with geochemical and mineralogical characteristics of the main types of rocks which occur in the Ditrău massif area.

Also this paper contributed to understanding the importance of the parent rocks in pedogenesis and the way physicochemical and mineralogical factors could control the fractionation and the migration of these elements during formation of the soil profile.

Secondary objectives of this theses, that may contribute to the knowledge base for further studies, are represented by assessing natural background radioactivity and outdoor radon levels in the Ditrău Massif area, associated to the presence of the naturally occurring radionuclides in soils in the context of increasing interest in monitoring radiation levels, respectively radon and their impact on human health.

The main type of soils formed on the alkaline rocks; according to the Romanian Soil Taxonomic Classification are lithosols, andosols, eutricambosols, districambosols, prepodzols, rendzinas, aluviosols, preluvisols, luvosol and gleysols.

The lithosols, andosols, prepozols, districambosols and eutricambosols cover most of the massif surface, being developed on the igneous rocks of the massif and metamorphic rocks that surround the Ditrău massif. Rendzina occupies a small area in the south western part of massif near the Lăzarea village and was formed on crystalline limestones (marbles) and dolomites. Preluvisols and luvosols are developed in the western edge of the study area on Pleistocene and Pliocene sedimentary formations, and Holocene formations in the Mureș Basin. Aluvisols are developed on small areas in the Ditrău, Jolotca, Putna Întunecoasă and Belcina brooks meadows. Gleysols are present in the Mureș valley meadow and in the submontane depression surrounding localities

Lăzarea and Chiruț. All these soils are young soils, with undeveloped soil profile, often short and rich in skeletal material represented by unaltered rock fragments.

70 soil samples were collected from sampling points distributed over the whole surface of the Ditrău alkaline massif, in relation with most representative rock types (approximately 10 soil sampling points for each type of rock). Additionally, rock samples were collected in each sampling point and field radiometric measurements were recorded. The outdoor gamma radiation levels - estimated as *gamma dose rate* was determined in air at 1 m above ground using a portable gamma monitor. Radon activity concentration in outdoor air was measured in the same points and in the same working conditions as the gamma dose rate, using a portable alpha radon monitor.

The analytical techniques employed for the investigation of soil and rock samples were: i) Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) for determination of REEs, U and Th concentrations in soil samples; ii) Gamma-ray spectrometry with high purity germanium detector for determination of uranium and thorium specific activities in soil and rock samples; iii) X-ray Powder Diffraction (XRD) for determination of mineralogical composition of soil; iii) Dispersive x-ray spectroscopy (EDXS) for determination of REEs, U and Th bearing minerals in rock samples. Physical-chemical parameters such as pH, respectively organic matter content were also determined for the soil samples.

The spatial distribution of the investigated elements (REE, U, Th) in soils developed on rocks of the alkaline massif was assessed through the elemental geochemical distribution maps. Additionally, distribution maps for pH, gamma dose and radon concentration have been built. The spatial point grid was built using the geographic coordinates for each sampling point, by attributing in each point individual values of REEs, U and Th contents, as well as the other measured parameters. *Topo to raster* is the interpolation method that was chosen to obtain the spatial distribution of rare earth elements in soils from the massif area. The software used for graphical representation and interpolation of the data is Arc GIS 9.3 from ESRI.

The REEs contents data show that the soils of the Ditrău alkaline massif are strongly enriched in light rare earth elements (from Ce to Eu) and depleted in heavy rare earth elements (from Gd to Lu) and yttrium. LREEs have a substantial contribution in establishing the total content of REEs in soils; approximately 90 per cent of the ΣREE is given by the LREEs. In all soil samples examined, the concentration of REEs decrease in the following order: Ce > La > Nd > Pr > Sm > Gd > Dy > Yb > Er > Eu > Ho > Tb > Tm >Lu. This abundance of REEs in soils is typical for the Ditrău alkaline massif; the rocks of massif are described as enriched in LREEs and depleted in HREEs. In addition, typical for rocks which occur in the Ditrău area are enrichment in cerium and depletion in lanthanum - the soils developed on these rocks reflect directly the same situation. The wide variations in REEs content indicated many differences in the concentration of REEs in soils studied, these differences being induced by the nature of the parent material. Relatively high levels of REE concentration in soil are genetically associated with mafic and ultramafic rocks and alkali igneous rocks.

In all LREEs geochemical maps three anomalous areas with high concentration of light rare elements are delineated, as follows: i) a first area placed in the north-eastern parts of the massif (Jolotca area) with the highest values for LREEs, especially cerium and lanthanum. Here, the secondary geochemical halos have direct filiations with biggest REE+Mo veins mineralization associated with ultramafic and mafic rocks. Except cerium, all other REEs have maximum concentration in soil samples from this area; ii) the second area with LREEs anomalies occupies a greater area covering central, southern and south-western parts of massif. The apex of the LREEs anomalies (Prișica Peak) is associated with metasomatic syenites enriched in REE, U, Th, Zr. The largest number of LREEs anomalies (extending in south - west) are typical for the external zone of the massif with soils formed on alkali-syenites and nepheline-syenites and essexites with gradual transitions between them. In addition, the same LREEs geochemical halo emphasizes the intermediate zone represented by essexites, alkali-syenites cut by nepheline-syenite veins that were hybridized and metasomatically transformed. Small REE, Th, Zr, Nb veins and disseminated mineralization occur in this area; iii) the last area located in the north eastern part of massif, where LREEs anomalies in soil were generated by occurrence of monazite, thorite, zircon, aeschynite in granitoids and muscovitized nepheline (liebenerite) syenites and alkali-feldspathic syenites.

In comparison with LREEs, the spatial distribution of HREEs and yttrium in soils of the massif show slight anomalies. In general, high levels of HREEs and Y in soils were observed to follow two trends given by the characteristics of rocks. First trend, strictly linked to the basicity of rocks, when HREEs and LREEs are correlated almost perfectly, was remarked in the north-western and central-western parts of the massif, associated with veins and disseminated REE mineralization (Jolotca, Ghiduț) in mafic and ultramafic rocks. The second trend is observed in the south eastern part of the massif, given by the position and genesis of syenitic and granitic rocks (quartz-syenite, aplite syenite) which are located in depth and developed beyond the surface boundary of massif, generating a prevailing enrichment in yttric mineralization.

The chondrite - normalized REE plots (grouped after type of bedrock) showed anomalies for cerium, europium, gadolinium and dysprosium for most soils in the sampling area. The negative Ce-anomaly was highlighted in the most-developed soils on basic rocks, hornfels, transformed syenite, granite, marble while the cerium positive anomalies are indicated in soil samples developed on schists. Except for soils formed on mafic and ultramafic rocks where values close to one, in other soil samples from the Ditrău massif europium has a negative anomaly (at different degrees), suggesting the typical situation from the fresh bedrocks (granite, syenite, schist). A significant number of soil samples from the Ditrău massif show positive Gd, Dy and Tb anomalies, these being associated with the presence of vein mineralizations Jolotca and Belcina.

Analytical data show that uranium and thorium content values present large variation limits in soil samples; enrichment of thorium is observed in most of the soil samples investigated. Also for uranium and thorium distribution in soils, one can easily note the interdependence with the type of parental rocks. The soils developed on granitoid rocks that occur in the north-eastern and eastern parts of the massif have the highest thorium content among all types of soils. Preferential concentration of thorium in soils is expressed by the wide variations of Th/U ratio. High uranium contents were determined in soil samples developed on syenite and nepheline syenite. For all types of soil the radioactive elements content increases from soils developed on basic to those developed on acidic rocks. A positive correlation between uranium and thorium occurs in almost all type of soils.

The concentration of ^{238}U and ^{232}Th determined in soil samples are in good agreement with in-situ radiometric measurements, gamma dose and radon emanation. The spatial distribution of these parameters shows some relationship to the petrography of the underlying rocks, especially to porphyritic K-feldspar granitoids and contact rocks; the higher values of annual individual effective dose equivalent was estimated only in points from the massif area characterized by the highest value of ^{232}Th and ^{238}U in soil samples associate with presence of REE+Th+U mineralizations. The correlation matrix between gamma dose rate, radon concentration and ^{238}U and ^{232}Th specific activities from soil samples suggests that ^{232}Th is the main contributor to outdoor gamma levels in the Ditrău massif area, followed by ^{238}U.

XRD analysis enabled the identification of minerals like zircon, thorite, allanite, monazite, pyrochlore, aeschynite, columbite, bastnäsite, in soil samples, in which REEs, U and Th occur as major or trace elements. The concentration of REEs, U and Th in soils from Ditrău massif is largely determined by the abundance of heavy minerals in rocks and just a small fraction from these elements is incorporated in major minerals (amphibole, plagioclase, epidote, cancrinite) that were disaggregated in the course of soil formation. Irregular distribution of these minerals directly influences the oscillation range of REEs, U and Th values in soil.

Except for soils developed on marble (Lăzarea zone), characterized by neutral reaction, soils from the Ditrău massif have mostly acidic or weakly acidic reaction. Organic matter contents in soil samples are relatively low to medium. The weak fractionation of REEs, in soils from the investigated area is indicated by the low correlations between pH, organic matter and total content of LREEs. However, there is a better correlation between ΣHREE – pH and ΣHREE – O.M. suggesting the HREEs have a higher mobility being more complexed and more adsorbed than LREEs on organic matter. The ratio ΣLREE/ΣHREE varies regardless of the soil types within larger limits suggesting, likewise, the preferential enrichment of soils in LREEs and depletion of soils in HREEs. This observation is also substantiated by the ratio (La/Yb)cn, which has a strong correlation with ΣLREE/ΣHREE.

The low correlations with organic matter content and pH values has been indicated also by uranium and thorium, being slightly better for uranium in agreement with the greater mobility of uranium (soluble in the U^{+6} state) in environmental conditions.

All these data are showing that the soil profile was formed in situ. The actual values of REEs, U and Th in soil directly reflect the rates of elemental depletion during bedrock weathering and disintegration attending pedogenesis. The high concentration of REEs, U and Th in soil samples are associated with mineralization areas and are given by the presence of minerals very strongly resistant to weathering, e.g. monazite, zircon, titanite, allanite, rutile, garnet, apatite, columbo - tantalite, a.s.o., thus explaining the correlation pattern. In soils devoid of strong REEs, U and Th geochemical halos, REEs reflect the situation from the rocks where these elements are concentrated in major silicates such as plagioclase feldspar, feldspathoids, epidote, and hornblende. The distribution of REEs, U and Th in soils indicated there does not support the direct association between soil type and degree of their concentration, being noticed, however, a trend of REEs enrichment in soils developed on basic and ultrabasic rocks in comparison with those developed on acidic rocks, which are enriched in uranium and thorium. The distribution of REEs, U and Th in soils is primarily controlled by the distribution of the accessory minerals in bedrocks, and subordinately by the physical and chemical stability of these minerals during the pedogenetic process.