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**LITHIUM MOBILITY AND BIOAVAILABILITY ON THE GRANITE –
SOIL BOUNDARY IN AN ACIDIFIED ENVIRONMENT**

INTRODUCTION

The Karkonosze block (S-W Poland) is composed of felsic rocks. It is known as a Li, Be, U, REE, Sn, W, Mo bearing massif, however the ore mineralization that appears within the Karkonosze – Iżera Block, includes many others elements: Ag, As, Au, B, Bi, Cu, F, Pb, Sb, and Th. Some of the elements are micronutrients and some of them are phytotoxic. From the standpoint of a potential hazard to human health, all of these elements are toxic in excess, and some of them even in very small doses. The Karkonosze massif and its mountain soil cover seems to be an especially good natural laboratory for studying mobilization and cycling of trace elements within alteration profiles developed in an acid environment. Groundwater in this area is poorly mineralized. The most common ground and surface water is of the type HCO₃–SO₄–Ca–Mg and SO₄–Ca–Mg. The pH of groundwater varies from very low (3.2) to nearly neutral (6.5). The source of the soil acidification is the weathering of the ore minerals, which influences not only the pH but also the composition of the groundwater. Another source is acid rain. Both weathering and acid rain deliver to the soil SO₄ and NO₃ ions and significant amounts of heavy metals and aluminium. The knowledge of element mobility in the rocks, water and soils of this area is very poor. The existing data deal with “total concentration” of some of the mentioned trace elements in the profiles of the Sudetic soils, but data concerning bioavailability of the elements in the considered region are absent.

EXPERIMENTAL

In order to show the mobility on the boundary rock-soil the following data have been collected from the vertical profile granite-soil in Szklarska Poręba Huta quarry: lithium concentration in fresh (13.4 ppm), hydrothermally altered, weathered rock (4.9 ppm) and soil horizons covering the rock (6.8 – 37.6 ppm).

Sequential extraction has been applied to determine the mobility of the trace elements in the soils and the bioavailability of the trace elements in the investigated environment. The soils have been collected from each genetic horizon. The

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investigations of the soil samples comprised pH_{KCl} and $\text{pH}_{\text{H}_2\text{O}}$ measurements, and determination of the mineralogical and trace element compositions (XRA, ICP MS). The organic carbon content has been determined for the whole sample. Sequential extraction of the >1mm fraction in the selected samples from each soil horizon has been carried out according to the following stepwise procedure (Kersten and Förstner, 1987): step I: ammonium acetate extraction (ion exchange fraction), step II: dilute acetic acid extraction (carbonate fraction), step III : hydroxylamine / acetic acid extraction (reducible fraction), step IV: hydrogen peroxide extraction (organic / sulphidic fraction), step V: hot concentrated nitric acid extraction (residual fraction).The composition of the extracted solution was determined by means of ICP MS. The results are shown on figure 1.

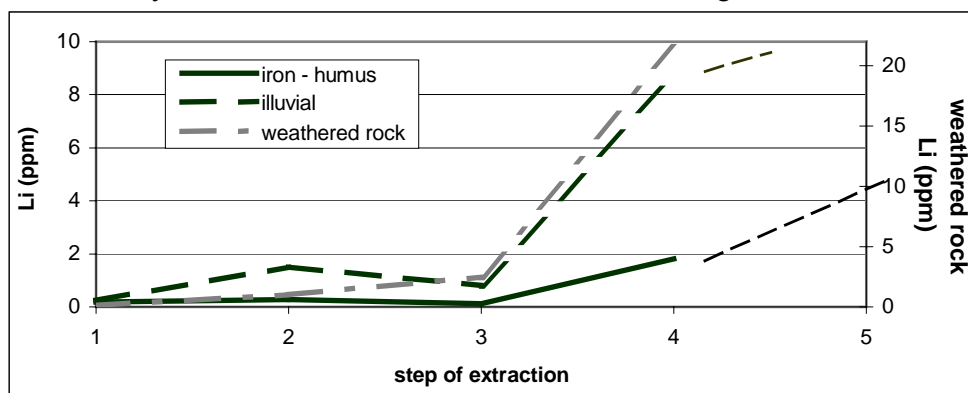


Fig.1 Lithium concentration in soil fractions (the scale on the left show concentration for iron-humus and illuvial, on the right for weathered rock).

The change in lithium concentration in relation to concentration of the less mobile element in both the soil horizons the parental rock was determined using Nesbitt and Markovics (1997) formula:

$$\% \text{ change in ratio} = [(R_s - R_p) / R_p] * 100$$

where R means lithium ratio to the most immobile element in the environment (hier Ti), the subscripted *s* represents soil and *p* fresh, parent rock (covered by soil). Lithium behaviour was determined using titanium content in all kinds of rocks from the quarry: fresh granite, weathered – hydrothermally changed granite and pegmatite. The results presents figure 2.

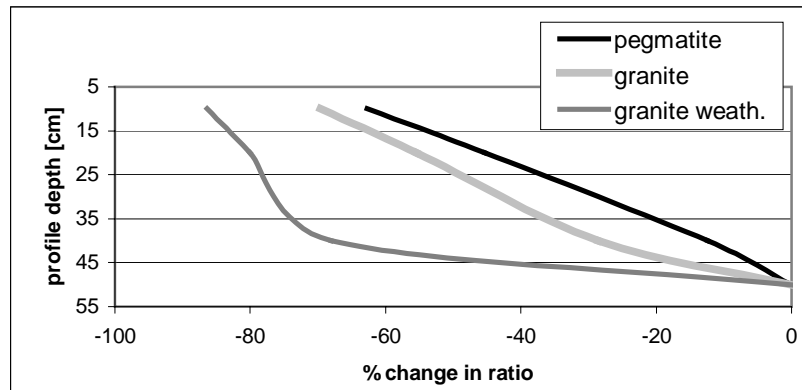


Fig.2 Percentage changes to elemental ratios Li/Ti

DISCUSSION AND CONCLUSION

There are two lithium bearing mineral groups in the investigated system: feldspars and micas. The dissolution rates of the last ones are at least one magnitude higher in acidic environment. The absolute lithium mobility is high in both soil and rock profile. The soils are enriched in Li comparing to rocks up to four times. Lithium concentration in bioavailable fractions is negligible. Its concentration grows in organic / sulphidic and residual fractions. The difference in the rate of leaching process from all of the rocks type is well visible. Lithium and titanium gathered in biotite and are released due to weathering processes. Titanium however released in early stage of alteration process is precipitated before it is transported out of the sample, so it behaves like immobile element. The impoverishment of the rocks in lithium (60-80%) correlates well with the degree of biotite chloritization in the samples. The array of increasing amount of decayed biotite is the following: fresh granite, pegmatite, weathered granite. The presented preliminary results on lithium mobility are the input data for the model of lithium cycling on the boundary between felsic rock and formed from the rock soil.

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