CZECH UNIVERSITY OF LIFE SCIENCES, PRAGUE

FACULTY OF ENVIRONMENTAL SCIENCES

DEPARTMENT OF ENVIRONMENTAL GEOSCIENCES

MASTER OF SCIENCE (M.Sc.) THESIS

Mobility and biogeochemical cycling of base cations (Ca and Mg) during weathering processes in a sensitive forest ecosystem, Lysina, Slavkov Forest, Czech Republic

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Prague 2014

CZECH UNIVERSITY OF LIFE SCIENCES PRAGUE

Department of Environmental Geosciences

Faculty of Environmental Sciences

DIPLOMA THESIS ASSIGNMENT

Nwaogu Chukwudi

Thesis title

Mobility a bio-geochemical cycling of base cations (Ca and Mg) during weathering processes in sensitive forest ecosystem

Objectives of thesis

This project will focus on the quantification of natural weathering fluxes of major base cations (Ca and Mg) within the sensitive forest ecosystem environment, developed on naturally base poor bedrock composed of granites (i.e. Mg and Ca depleted igneous rocks) at the study site of the Slavkov Forest (Lysina, CZ). Within the project we will investigate changes in Ca and Mg concentrations as a function of depth, throughout a complete weathering profile (i.e. regolith), using samples of soil profiles but also recently recovered drill core material reaching depths up to 30 meters below the surface. These unique sample materials will allow to study the dynamics of the studied elements release from rocks during weathering and it subsequent uptake by plants and vegetation, and its deposition/mobilization within the organic-rich and mineral soils.

Methodology

In terms of methods, this project will employ state-of-the-art facilities such as the metal-free geochemical laboratories used for sample digestion and preparation (at CGS), and modern analytical instrumentation such as ICP-OES, available at KGEV, CZU. Specifically, we will normalize the concentration of Ni and Cr measured in rock/soil/organic samples to an immobile element such as zirconium (Zr) or titanium (Ti) which will allow us to quantify the rates of release of base cations (Ca and Mg) to the soil system and vegetation pools at our study site. These results, in turn, will have implications for our understanding of the biogeochemical cycle of Ca and Mg in the environment and the negative effects of base cations loss for the growth and overall health of the local forest ecosystem (composted mostly of Norwegian spruce, and oak species).

Schedule for processing

January - February 2013: Study of references and literature
March - April 2013: Examination of the drill core, and preparation of IGA proposal
May - September 2013: Data collection and laboratory work
October - December 2013: Data analysis, modeling, and Thesis write up
Thesis submission April 2014

The proposed extent of the thesis

Anticipated extent of this Master thesis is set at about 50 pages of the written text.

Keywords

base cations, forest ecosystem, weathering processes, acidification

Recommended information sources

Hruška J. and Krám P. (2003) Modelling long-term changes in stream water and soil chemistry in catchments with contrasting vulnerability to acidification (Lysina and Pluhuv Bor, Czech Republic). Hydrology and Earth System Sciences 7, 525-539.

Brantley S.L., Goldhaber M.B. and Ragnarsdottir K.V. (2007) Crossing disciplines and scales to understand the Critical Zone. Elements, Vol. 3, pp. 307-314.

Kram, P., Hruška, J. and Shanley J.B. (2012) Streamwater chemistry in three contrasting monolithologic Czech catchments, Applied Geochemistry, 27, 1854-1863.

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Electronic approval: January 21. 2014

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Electronic approval: January 22. 2014

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Dean

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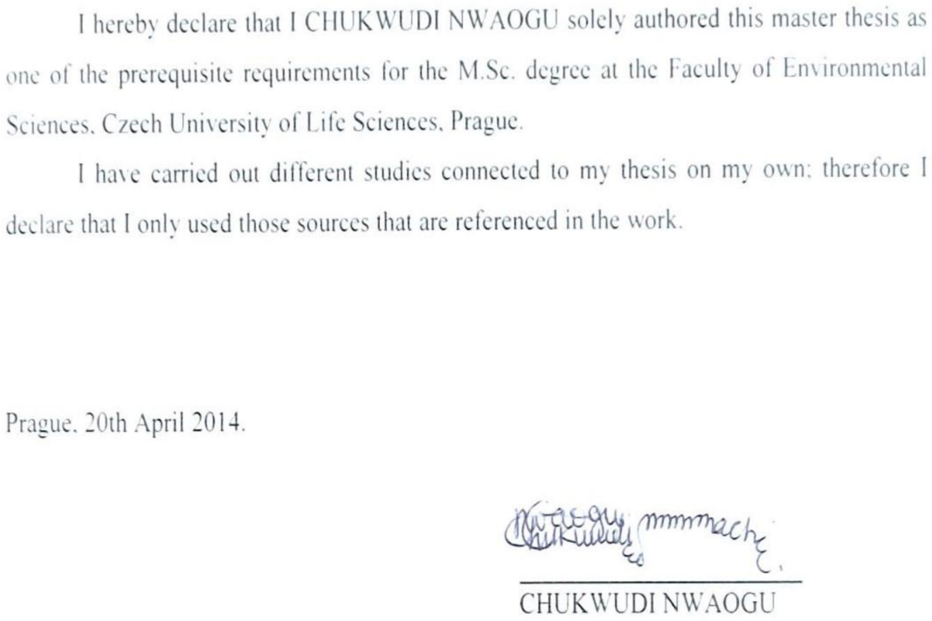
DECLARATION



I hereby declare that I CHUKWUDI NWAOGU solely authored this master thesis as one of the prerequisite requirements for the M.Sc. degree at the Faculty of Environmental Sciences, Czech University of Life Sciences, Prague.

I have carried out different studies connected to my thesis on my own; therefore I declare that I only used those sources that are referenced in the work.

Prague, 20th April 2014.

CHUKWUDI NWAOGU

ACKNOWLEDGEMENTS

The support of the IGA grant from the Czech University of Life Sciences (KGEV 42400/1312/3177), and the European Commission Project (FP7 SoilTrEC 244118, to the Czech Geological Survey) are acknowledged.

I hereby wish to express my appreciation and gratitude to my supervisor,
doc. Mgr. Juraj Farkaš, Ph.D. and co-supervisor, Dr. Pavel Krám for all guidance and contributions throughout the whole period. I am grateful to Anna Pereponova, Hana Šillerová, Dr. Veronika Štědrá, Dr. Tomáš Jarchovský, for their direct and indirect support.

Special thanks are extended to the Czech Geological Survey for giving me the space and materials for implementing and carrying out the experiment and analyses in their laboratories.

I would like to thank my family for supporting and encouraging me for this study abroad and to complete and write this thesis. Kudos! to my better-half, Mrs Modupeola Abike Chukwudi-Nwaogu. Nne Ed Tito China'ndu. Aya-mi (*mo ni fe e,: ahurumgi nanya: I love you*). I cannot thank you enough for you are one among zillion women.

I dedicate this thesis to the fountain of wisdom and the only provider, Jehovah -Jireh for ALL He has done.

ABSTRACT

There has been substantial evidence that atmospheric acid deposition has to a large extent depleted exchangeable pools of base cations in soils in Central Europe during the past decades (Hruška and Krám, 2003). This has detrimental effects of decreasing the capacity of the soils in the region to neutralize acidity. Mineral weathering has been of great succour through its significant and positive contribution in supplying the alkaline earth metals (such as Ca, Mg, Sr) readily available for plants use, and they also off-set and neutralise acidity in forest soils.

In this study we investigate the effect of weathering processes on selected alkaline earth metals (Ca, Mg, Sr, Ba), and their biogeochemical cycling and mobility at the base-poor granitic catchment Lysina, in the Slavkov Forest, Czech Republic. Samples were collected from a drill-core and a soil-pit, with depths reaching up to about 2500 cm and 150 cm, respectively. These samples were dried down, homogenized, weighed, dissolved via acid digestion and analysed for their elemental concentrations by ICP-OES at CULS, Prague. Normalized concentration profiles (i.e. tau values) of alkaline earth metals were generated as a function of depth through the regolith profile, using an immobile element (titanium, Ti) as a reference for the normalization (Brantley et al.2007,; Brimhall and Dietrich 1987). This approach allowed us to quantify the degree of depletion and/or enrichment of selected alkaline earth metal through the weathering profile.

Results showed that Ca, Mg, and Sr all experience significant “depletion” trends toward the top soil, whereas Ba revealed an “enrichment” profile at the shallower depths. Specifically, Ca was highly depleted closer to the organic-rich top soils (tau-values up to -0.97), and Mg also showed a depletion trend but with lower magnitudes (tau-values about -0.84). This observation supports the fact that Ca often out-competes Mg with respect to the intensity of element leaching from the soils and rocks due to weathering and biological processes. Similarly, the normalized weathering profile of Sr showed a “depletion” trend (tau-values about -0.74) that, however, is less pronounced compared to Ca or Mg. In contrast, the normalized weathering profile for Ba yielded a significant “enrichment” trend (with tau-values up to + 4 or 5) whose origin is not currently well understood.

Conclusively, our results from the acidified base-poor forest ecosystem show that the behaviour of alkali earth metals during weathering and soil formation follows a trend where Ca is leached most readily from the system, followed by Mg and Sr. The extremely negative tau-values of Ca, Mg and Sr trends in the upper part of the weathering profile (from -0.74 up to -0.97) are likely a consequence of the long-term and severe acid deposition history at our study site.

Key words: mobility, biogeochemical cycling, base cations, weathering, forest ecosystems, granitic soil, acidification, calcium and magnesium deficiency.

ABSTRAKT

Ve střední Evropě způsobila nadměrná depozice atmosferických kyselin v posledních desetiletích vyčerpání volných zásaditých kationtů v půdě (Hruška and Krám, 2003). To snižuje schopnost půdy neutralizovat její kyselost. Zvětrávání minerálů má naopak pozitivní vliv, neboť dochází k uvolňování kovů alkalických zemin (jako Ca, Mg, Sr). Tyto prvky jsou jak okamžitě dostupné pro rostliny, tak schopné neutralizovat kyselost lesních půd.

V této studii jsme se zabývali vlivem zvětrávacích procesů na vybrané prvky alkalických zemin (Ca, Mg, Sr, Ba), a na jejich biochemický cyklus a dostupnost na bazicky chudém granitickém stanovišťi. K tomu byla vybrána lokalita Lysina ve Slavkovském lese na severozápadě České republiky. Vzorky byly získány z horninového vrtu a půdní sondy hluboké 150 cm respektive 2500 cm. Tyto vzorky byly následně vysušeny, homogenizovány a zváženy. Koncentrace jednotlivých prvků byla zjišťována pomocí metody ICP-OES. Normalizované profily koncentrací zjišťovaných prvků byly vygenerovány jako funkce hloubky napříč půdním profilem. Pro normalizaci byly jako referenční využity hodnoty imobilního prvku titania (Brantley et al.2007,; Brimhall and Dietrich 1987). Tento přístup nám umožnil kvantifikovat "vyčerpání" nebo naopak "obohacení" vybranými prvky napříč profilem zvětrávání.

Z výsledků je zřejmé, že Ca, Mg a Sr vykazují trend "vyčerpání" směrem k ornici, naproti tomu Ba "obohacuje" profil směrem do nižších hloubek. Zvášťě Ca bylo vysoce vyčerpáno blížeji k organicky bohaté svrchní vrstvě půdy (T > -0,97), stejně tak Mg, ten ovšem v nižší míře(T±-0,84). Toto zjištění podporuje fakt, že Ca často vytěsní Mg s ohledem na intenzitu částic vyloučených z půdy a hornin skrze zvětrávání a biologické procesy. Podobně tak normalizovaný profil zvětrávání Sr ukázal trend vyčerpání (T±-0,74). Ten je však v porovnání s Ca nebo Mg méně výrazný. Naopak, profil zvětrávání Ba vykazoval trend "obohacení"(T>+ 4 nebo 5), což nebylo dosud dostatečně vysvětleno.

Naše výsledky na překyseleném bazicky chudém lesním ekosystému ukazují, že chování kovů alkalických zemin během zvětrávání a formování půd vykazuje trend, kde vápník je vyplaven ze systému nejsnadněji, následován hořčíkem a stronciem. Extrémně negativní hodnoty T v trendech všech tří prvků ve srchní vrstvě profilu zvětrávání (od -0.74 do -0.97) jsou pravděpodobně důsledkem dlouhodobé a výrazné acidifikace v průběhu minulého století.

Klíčová slova: dostupnost, biochemický cyklus, bazické kationty, zvětrávání, lesní ekosystémy, granitická půda, okyselení, nedostatek Ca a Mg.

1. INTRODUCTION

Naturally base-poor forests are particularly sensitive to environmental perturbations including phenomena such as anthropogenic input of acid compounds, contamination of forest soils by toxic metals, and/or excessive timber harvesting. These human-induced processes accelerate the export of base-cations from the ecosystem, causing acidification and degradation of soils, which in turn have negative influence on the overall health and productivity of the affected forest. Temperate coniferous forests developed on naturally base-poor substrates (i.e. bedrocks depleted in Ca and Mg), located in the industrialized parts of the Czech Republic are particularly prone to the above phenomena and their negative effects. Hence, a better understading of elemental fluxes and geochemical cycling of the major base cations, and toxic metals, in naturally base-poor forests is of primary importance for sustainable forest management strategies.

The primary goal of this project is to systematically investigate the mobility and bio-geochemical cycling of major base cations (Ca^{2+}, Mg^{2+}), and selected toxic metals (Ni and Cr), during weathering processes in a distinctive forest ecosystems located near the town Marienbad (Marianske Lazne) in western Bohemia, about 120 km west of Prague (Fig. 1), (Krám et al., 2012). The study site is a grantitic catchment 'Lysina' located in the Slavkov Forest, which is a region of a Protected Landscape Area (CHKO Slavkovsky les). Long-term environmental monitoring studies performed in this region showed that stream waters draining the Slavkov Forest experienced marked declines of the sulphuric (SO_4^{2-}) and nitric (NO_3^-) anions since the 1990s, and a concomitant increase of stream water pH and alkalinity (Fig 2), caused mainly due to a long-term decline in atmospheric acidic deposition (Shanley et al. 2004) linked to lower anthropogenic SO_2 emissions from fossil fuel burning.

These long-term improvements in stream water carbonate chemistry at the Slavkov Forest are, however, associated with a continuous decline in the concentrations of major base cations, Ca^{2+} and Mg^{2+}, in local runoff (Fig. 2). This ongoing leaching and permanent loss of base cations from the soil-water-plant system further lowers the already deteriorated and naturally limited 'buffering' capacity of the local soils, which certainly may have negative impacts on the forest health and its productivity in near future, unless suitable strategies are put in place to ameliorate this ongoing ‘leaching’ trend. This continuing release of Ca^{2+} and Mg^{2+} from soils, and their export by stream waters, is related mostly to decline of anthropogenic sulphate (SO_4^{2-}) concentrations in drainage waters (Hruška and Krám 2003) and also to ‘inertia’ of the soil-water-plant system and ‘time-lag’ of certain bio-geochemical processes that control the pH and alkalinity budget in the soils. Therefore it is vital to fully understand these processes, and possible sources and biogeochemical pathways of the base cations and toxic metals in naturally base-poor forests.

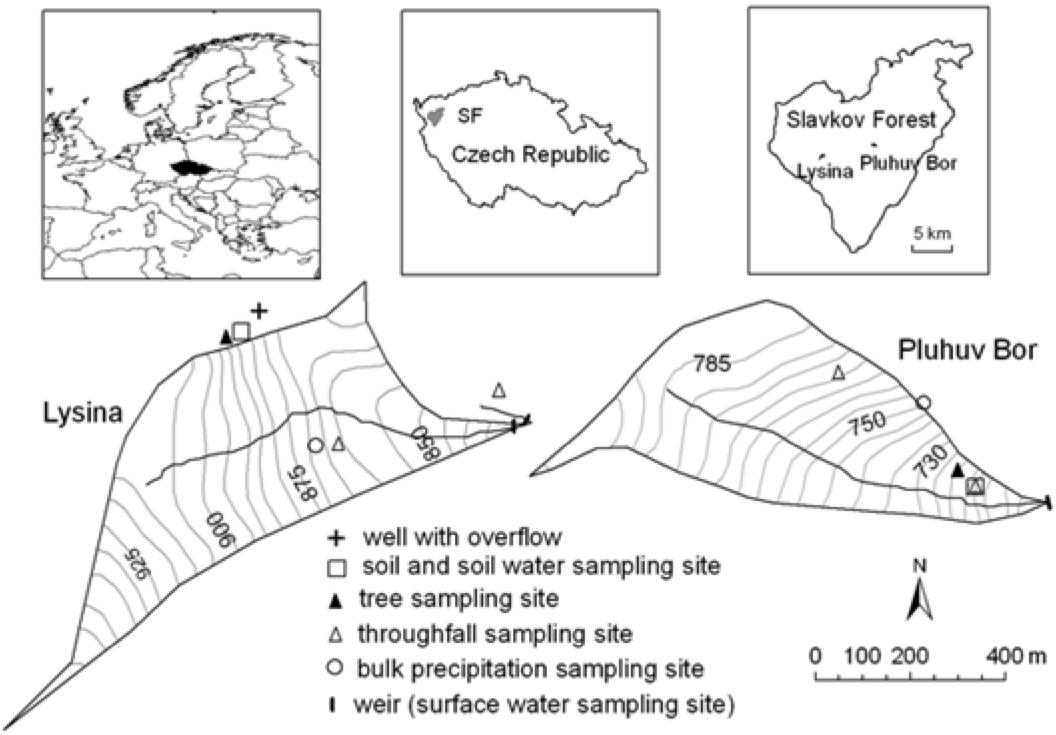


Fig. 1. *Upper panels: map of Europe, map of the Czech Republic showing the Slavkov Forest (SF), map of the Slavkov Forest showing the study catchment. Lower panel: topographic maps of the Lysina and Pluhův Bor catchments showing the major stream channels and the major sampling locations (Krám et al. 2012).*

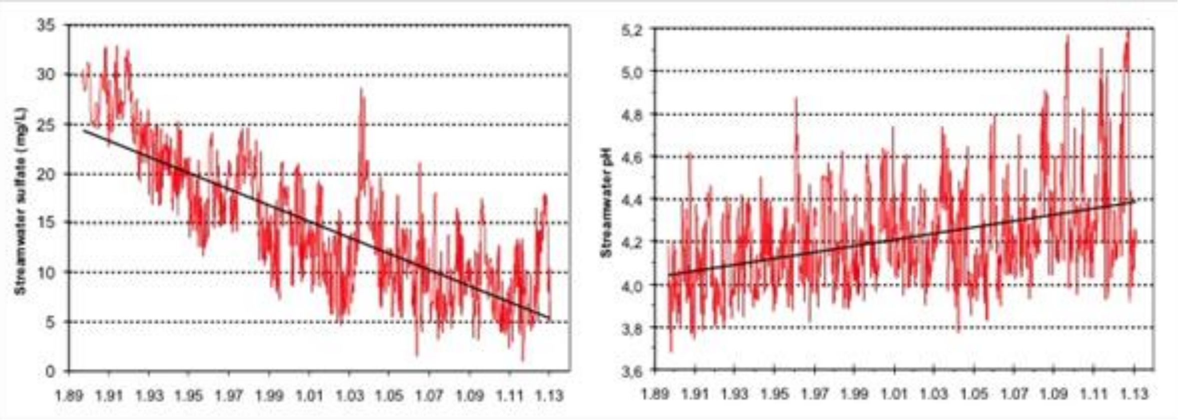


Fig. 2. Temporal patterns of stream water sulphate and pH in weekly time step at Lysina between September 1989 and March 2013 (Krám et al., unpublished data).

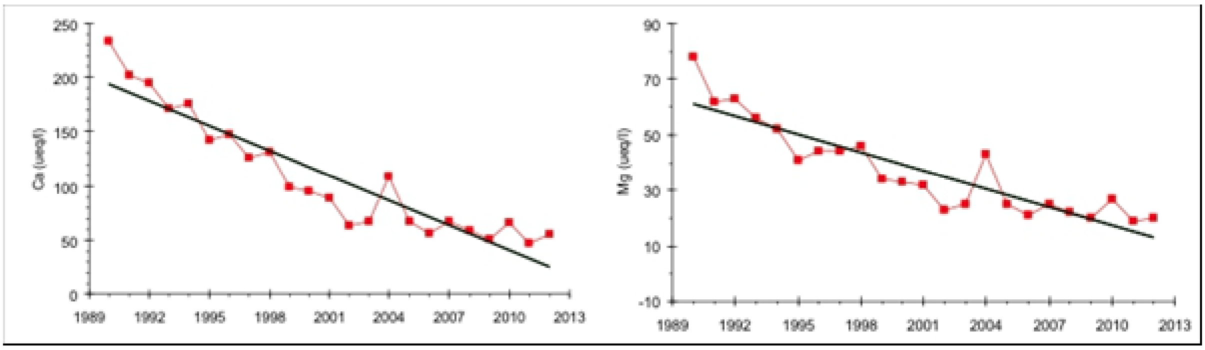


Fig. 3. Annual mean discharge-weighted concentrations of stream water calcium and magnesium at Lysina in 1990-2012 (Krám et al., unpublished data).

1.1 Project Aim/Objectives

This project aimed at investigating the mobility and bio-geochemical pathways of major base cations (Ca, Mg), and toxic metals (Ni, Cr), during weathering processes in the geologically distinctive forest ecosystems which is underlain by granitic rocks. The primary goal of this project is to generate continuous weathering profiles for elements of vital interest (Ca, Mg, Cr and Ni), based on the analysis of elemental concentrations in the samples of rocks/soils that were recently recovered by a drill core at this geologically unique site (i.e., the granitic Lysina). The region of the

Slavkov Forest was not glaciated and is therefore overlain by a thick and relatively well-developed regolith (i.e., a portion of fractured/weathered rocks that rest on unweathered bedrock). The scientific drilling at our study site was accomplished only recently, in summer 2012, and was funded via the European 'SoilTrEC' project (http://www.soiltrec.eu/; Banwart et al. 2012). The drill core reached a depth exceeding 25 meters below the surface, and thus the recovered sample materials cover a significant portion of the local 'weathering profile', with potentially well-defined concentration gradients of Ca, Mg, Sr, Ba, Ni, Cr, and other elements controlled by the weathering intensity and biological activity at our site. The profiles of elemental concentrations, as a function of depth, generated by this project in turn allowed us to quantify the rate of release (or accumulation) of the specific element along the weathering profile. This knowledge helps in the identification of the zone(s) of maximum leaching and/or accumulation of the element of interest during the weathering and/or biological uptake by forest biomass, which has implications for possible sources and bio-availability of these elements for the growth of local forest.

Project Aim/Objectives Summarized as follows:

Aim:

To assess the fluxes and the biogeochemical pathways during weathering and biological uptake of the two base cations (Ca^{2+} and Mg^{2+}) in the poor- forest ecosystem.

Objectives:

- 1. To determine the rate of Ca and Mg mobility in the study area
- 2. To examine the biogeochemical processes controlling the divalent base cations in the study site.
- 3. To investigate the effects of Ca and Mg deficiency on the forest ecosystem.
- 4. To generate continuous weathering profiles for the base cations and alkaline earth metals in a granitic soil.
- 5. To identify and examine the weathering profiles of other elements of interest in this study area.

1.2 Research Questions:

- i. Do the weathering processes actually affect the availability of mineral nutrients readily for plants' use, and to what extent?
- ii. Which other soil element(s) apart from Ca and Mg play(s) significant role at Lysina forest ecosystem?
- iii. Is historic acid atmospheric deposition a very important factor for leaching and trend of these elements in weathering profile?
- iv. Do the soil compositions have any effects on the elements depletion or replenishment?
- v. What are the likely environmental management practices or scientific techniques that can be employed to ameliorate the enhanced leaching of base cations, or the accumulation of toxic metals?

2. LITERATURE REVIEW

2.1 The biogeochemical properties of calcium (Ca) and magnesium (Mg)

Biogeochemical cycling involves a continuing exchange of chemical elements between the biota and the physical environment within an ecosystem. Therefore, all biogeochemical cycles show strong interrelations and dependencies with site-internal and external factors. Specifically, soil properties control the physical, chemical and biological conditions in the rooting zone and these thus represent the site-interference factors. External factors include climate, atmospheric pollutants and forest management. The cycling of the various nutrients and non-nutrient elements in an ecosystem is highly interrelated. For a given element, the nutritional status of a tree stand depends on the requirement and the uptake. Requirement can be defined as the annual element increment associated with all tree components (bole, bark, branches and roots) plus the current foliage production. In addition to requirement, uptake includes also the return (litterfall, stemflow, and crown wash which are also termed leaching). Rates of internal recycling can be estimated from the difference, i.e. 'requirement minus uptake'. Calcium (Ca) and magnesium (Mg) are among the essential macro-elements for plant growth and they occupy pivotal position in keeping the plant cell structure, resistance of adversity stresses (such as drought, cold shock, high temperature, and diseases), and also signal transduction (Navrátil, et al., 2002, 2003 and 2007). Calcium is a member of the alkaline earth group (Be, Mg, Ca, Sr, Ba, Ra) of elements characterized by strong metallic properties. Because of their electronic configuration (ns2, where n is the period) and very high third-stage ionization energies, elements in this group are predominantly divalent with a tendency toward covalency in the lighter elements (Be and Mg) (Greenwood & Earnshaw 1984). Calcium is the most common of the alkaline earth elements in Earth's crust (Wedepohl, 1995). It comprises about 3.85% of the mass of the upper continental crust (Wedepohl, 1995), and is common in igneous rocks, such as granites, characteristic of the continental crust, but is considerably more abundant in mafic rocks such as basalts, which are more common in the oceanic crust (Bowen 1979).

Magnesium (Mg) is a major element in most (especially mafic or ultramafic) rocks such as basalts or serpentines. The main magnesium (Mg) bearing minerals are olivine, orthopyroxene, clinopyroxene, serpentinite, talc, brucite, chlorite, pyrope,

amphiboles, biotite, tourmaline, magnesite and spinel. During the weathering of rocks Mg readily dissolves in weathering solutions and enters the hydrosphere.
Calcium is also relatively easily weathered as a soluble cation from both primary and secondary minerals, the rate largely depending on solution pH. When liberated, it moves readily into the soil solution where it may be adsorbed onto the cation exchange complex, taken up by plants or microbial organisms, or leached through the soil profile. Ca is adsorbed strongly to clays and humates compared with other metallic cations. This is because of its divalent charge, relative abundance and modest extent of hydration. Therefore, inorganic Ca exists in the rock-soil component of terrestrial ecosystems as a structural component of primary and secondary minerals, on the exchange complexes, and as a cation in soil solutions.

As to the atmospheric deposition, Krám et al. (1997) reported a bulk precipitation flux of Mg of 4.4 meq.m^{-2}.yr^{-1} at the granitic catchment Lysina in 1993. Similarly, it is revealed that the rates of total Mg deposition range between 1.6 and 21.4 meq.m^{-2}.yr^{-1} with wet and dry deposition being the predominant processes. According to Likens et al (1998), the main sources of Mg in the atmosphere are sea salts (at marine areas), mineral dusts (industrial and natural) and fly ashes (from point-source emissions). In support, Armbruster et al. (2002) reported an overview of European sites (including Czech sites) with Mg throughfall fluxes ranging from 1.9 to184 meq.m^{-2}.yr^{-1}. High throughfall fluxes at some Czech sites were due to local alkaline dust emissions. Krám et al. (1997) stated that there is greater Mg throughfall fluxes of 33.8 meq.m^{-2}.yr^{-1} on a catchment with bedrock rich in Mg (serpentinite) compared to 20.4 meq.m^{-2}.yr^{-1} on a catchment with bedrock low in Mg (granite). Enhanced fluxes of Mg in throughfall with respect to bulk precipitation are due to both dry deposition to the canopy and leaching from plant tissues (Armbruster et al. 2002).

In reference to Ca, due to its ionic charge, it is not readily lost from soils having significant cation exchange capacity, except in acidic soils with elevated concentrations of exchangeable aluminium. Therefore, Ca is usually the most abundant of the alkali and alkaline earth elements on the soil exchange complex, and is important in the regulation of soil pH (Bowen 1979). Calcium is not leached readily from living foliage due to its relative immobility in pectates and on membranes – a distinct contrast with K. Thus, in forest ecosystems Ca typically cycles between plants and soil through uptake litterfall- mineralization processes.

As to the Mg biogeochemistry, magnesium is known as a critical structural component of the chlorophyll molecule and is necessary for functioning of plant enzymes to produce carbohydrates and fats. Magnesium deficient plants appear chlorotic, show yellowing between veins of older leaves; leaves may drop. However extreme amounts of Mg may cause defects of vegetation growth and dwarf forms of plants known as nanism (Ende, et al., 1997). At granitic sites, biotite was likely the most important source of Mg in addition to secondary minerals such as chlorites.

2.2 Biogeochemistry of base cations in forest ecosystem

Mg deficiency like Ca has played a prominent role in recent forest decline phenomena at industrialized sites. In order to understand the difference in Mg supply in a site and temporal development, a thorough analysis of the biogeochemistry cycling of this element and major processes is necessary.

Bolou-Bi, et al (2012) denoted that in forest ecosystems, chemical weathering of silicate rocks release various macronutrients (e.g. Mg, Ca, and K) and micronutrients (e.g. Fe, Mn and B) as bio-available forms in soils and sustain plant growth in non-fertilized ecosystems. When the soil is in steady state, a simple input– output budget provides an estimate of the mineral weathering rate, for a given element, following the equation:

Weathering (W) = Accumulation in forest biomass (B) + Leaching in seepage water (L) - Atmospheric deposition (D). (That is, W=B+L-D).

However, most forest soils are not at steady state, especially when they are impacted by forest management and/or acid deposition. Indeed, plants associated with microbiota during their growth, may enhance silicate weathering rates (Benedetti et al., 1994; Bormann et al., 1998; Moulton et al., 2000; Landeweert et al., 2001; Uroz et al., 2009) through biological processes (root uptake + accumulation in biomass). During mineral weathering process, the Mg^{2+} cation, released from minerals in soil solutions, can be taken up by roots and stored in vegetation over short (month) or longer (hundreds of years) periods. Magnesium in plants ultimately returns to soils after decomposition, and possibly to streams. Zakharova et al. (2007) for example estimated that litter degradation would be responsible for 10–40% of dissolved Mg and Ca fluxes in boreal Russian rivers. However, the quantification of vegetation impact on silicate weathering and dissolved cation content in streamwater remain understudied.

2.3 The temporal dynamics of base cations in the granitic-acidic soils

In a study on acidification and recovery of soil at a heavily impacted forest catchment at Lysina, Czech Republic, applying SAFE modelling and field results, Navrátil, et al. (2007) revealed that despite large emission reductions in the 1990s, the Lysina catchment still suffers from the very high loads of acid deposition of the past and high uptake of base cations by aggrading biomass in planted Norway spruce monocultures. According to this research, soil recovery depends on future deposition loads, base cation deposition, and on forest management. A report was recorded on changes in the normative mineralogy and rates of calcium (Ca) and magnesium (Mg) loss from the uppermost mineral soil horizon due to chemical weathering for five soil profiles forming a 5276-year-old chronosequence (Starr et al. 2006). According to Starr et al. (2006) these two elements (Ca and Mg) are important plant nutrients and acid buffering constituents of the soil.

In view of a sustainable forest management, it is important to characterize the dynamics of major nutrients, such as Ca, Mg and K, in these forest soils. The fraction of those cations occupying the cation exchange capacity (CEC) is a measurement of their relative storage in soil and thus of their potential availability for tree nutrition. In acidic soils, the exchange reactions (adsorption/desorption reactions) between the soil solution and the exchange site are mainly dominated by element concentration in solution, inputs of acidity, speciation of Al and ionic strength of the soil solution (Ross et al. 2008). Although the chemistry of soil solutions reacts rapidly with the seasonal changes (Ranger et al. 2001; Vestin et al. 2008), it is generally admitted that the quantity of exchangeable cations is relatively stable or evolves very slowly in the time (over a 10 year period), due to soil acidification process (Johnson et al. 1990; Gbondo-Tugbawa and Driscoll 2003; Courchesne et al. 2005). However, the following studies have reported a weak decline (less than 50%) in the exchangeable nutrients (Ca, Mg and K) between late winter and summer in bulk soil of forest ecosystems (Haines and Cleveland 1981; Kelly and Mays 1999). These observations suggest thus that the stock of exchangeable nutrients can be influenced by the seasonal variations, particularly during the growing season when the nutrient uptake by vegetation is important.

Following Drever (1994) the main parameters that could influence the calcium, magnesium and sodium concentrations in waters draining granitic environment are: (i) trace calcite, halite and fluorite dissolution, (ii) the preferential weathering of trace calcic silicates, apatite and the selective weathering of calcic plagioclases, (iii) the released of calcium from soil exchange site leaching and from biomass decrease, and (iv) atmospheric inputs. Due to its great solubility, the dissolution of calcite present in certain granitic rock, even at trace levels, could strongly influence the calcium concentration in stream waters (White et al. 1999).

2.4 The effects of soil age and vegetation

The losses of Ca and Mg increased with soil age but at a decreasing rate. A study conducted in the glaciofluvial (esker) deposit in the coastal region of the Gulf of Bothnia in Finland, it was indicated that Ca and Mg losses for the youngest soil were 3.3 and 1.8 mol m^{-2} yr^{-1} respectively; corresponding values for the oldest soil were 10.6 and 10.5 mol m^{-2} yr^{-1}. Mean rates of loss for the youngest soil were 10 and 5 mmol m^2/ yr for Ca and Mg respectively, and corresponding values for the oldest soil were 2 mmol m^2 /yr for both Ca and Mg (Starr et al.2006).

A decrease in plant biomass could explain high calcium export at the catchment scale. As a nutrient, calcium is incorporated into terrestrial plants to a much greater extent than sodium. The natural uptake of calcium by plants and lichens (Likens and Borman, 1995; Prieto et al., 1997) contributes to depletion of calcium in surface waters. However, this process is reversible and the mass destruction of vegetation by, for example, fire or disease, can lead to elevated export of calcium in runoff.

2.5 The anthropogenic activities and ecological forces as the controls of base cations

The export of calcium, magnesium, and potassium in stream water exceeds inputs of these cations in precipitation in a variety of ecosystems (Federer et al, 1989, Likens and Bormann, 1995). The gradual loss of base cations from soils is a natural feature of weathering and pedogenesis. In addition, however, the loss of calcium and other base cations from soils is accelerated by human action, in more and less direct ways.

Over the past two decades, numerous studies have raised concerns about calcium (Ca) depletion in forest soils of the eastern United States (Likens et al., 1998; Huntington et al., 2000; Yanai et al., 2005). In many forests, this depletion has been well documented. For example, Likens et al. (1998) estimated a loss of 397–461 kg ha^{-1} of total Ca from the soil at Hubbard Brook Experimental Forest in New Hampshire between 1965 and 1992. In a 60–80-year-old southern Piedmont forest in Georgia, Huntington et al. (2000) estimated that the soil Ca depletion rate was 12.8 kg ha^{-1} year^{-1}. Calcium depletion has been attributed to leaching caused by acid deposition (Lawrence et al., 1995; Likens et al., 1996) and uptake and sequestering in woody biomass (Johnson and Todd, 1990; Huntington et al., 2000). The ecological consequences of soil Ca depletion could be devastating since long-term forest ecosystem health and sustainability have been closely linked to pools of available Ca in the soil (Graveland et al., 1994; NAPAP, 1998; Driscoll et al., 2001; Hamburg et al., 2003).

According to Krám et al (1997), if strong acid inputs exceed both weathering release and net exchange of base cations, increases in the concentrations of H$^+$ or Al in drainage water will result. Assimilation of Ca, Mg and K by forest vegetation, which may be enhanced by elevated inputs of atmospheric nitrogen-oxide compounds, can also deplete soil pools of exchangeable base cations on sites with slow weathering rates. Over all, there is evidence of depletion of available pools of base cations from soil in regions impacted by acidic deposition.

2.5.1 Acid deposition and effects on soil

Acidic deposition is the transfer of strong acids and acid-forming substances from the atmosphere to the surface of the Earth. Smith (1972) first identified acid deposition in the 19th century in England. The ecological effects of acid deposition emerged in the late 1960s and early 1970s in Sweden and around Scandinavia. The first report of acid deposition in the North America was made at Hubbard Brook Experimental Forest (HBEF) in the early 1960s. Over the last quarter of the past century scientists have identified acidification as a critical environmental stress that affects forested landscapes and aquatic ecosystems in North America, Europe, and Asia (Driscoll et al. 2001). Effects of acid deposition on terrestrial ecosystems include those on soils, vegetation, crops, animals and human health. Due to major negative effects of acidic deposition, North American and European legislative actions aimed at the recovery of damaged natural resources have resulted in recent decreases in both emissions and deposition of acidic S compounds.

The northwestern part of the Czech Republic experienced extraordinarily high acid atmospheric deposition in the second half of the 20th century, but this was followed by rapidly decreasing acid deposition during the 1990s (Hruška and Krám, 2003). A major buffering process in soils is the desorption of cations, which are bound to negatively charged soil particles. In ecosystems not impacted by acid deposition, the pool of base cations (calcium [Ca], magnesium [Mg], sodium [Na] and potassium [K] ions) is normally of considerable size. Soil acidification causes the soil content of base cations to be depleted and replaced by hydrogen and aluminium [Al] ions. Three base cations (Ca, Mg, K) are important nutrients for plants, but soil acidification can lead to their shortage and impaired forest growth (van Breemen. et al. 1984).

According to Driscoll et al. (2003), acidic deposition is comprised of sulphuric and nitric acids and ammonium derived from atmospheric emissions of sulphur dioxide, nitrogen oxides, and ammonia, respectively. These compounds are largely emitted to the atmosphere by the burning of fossil fuels and by agricultural activities. Acidic deposition has altered soil through depletion of labile pools of nutrient cations (i.e. calcium, magnesium), accumulation of sulphur and nitrogen, and the mobilization of elevated concentrations of inorganic monomeric aluminium to soil solutions in acid-sensitive areas. Acidic deposition leaches essential calcium from needles of red spruce, making this species more susceptible to freezing injury.

Recent research has shown that acidic deposition has caused chemical changes in soils in acid-sensitive ecosystems. Soils affected by acidic deposition have diminished ability to neutralize continuing inputs of strong acids, provide poorer growing conditions for vegetation, and extend the time needed for terrestrial and aquatic ecosystems to recover from acidic deposition. Acidic deposition has altered and continues to alter soils in parts of the Northeast, USA by: (1) depletion of calcium and other nutrient cations from the soil; (2) mobilization of inorganic monomeric aluminium into soil water; and (3) increasing the accumulation of sulphur and nitrogen in soil. Such changes can contribute to adverse impacts on forest health, and the toxicity of surface waters to sensitive biota (Lawrence et al., 1999).

2.5.2 Loss of calcium and other nutrient cations

Over the last century, acidic deposition has accelerated the loss of large amounts of available calcium from the acid-sensitive soil in New York and other acid-sensitive areas in the Northeast (Likens et al., 1996, 1998). Depletion occurs when nutrient cations are displaced from the soil by acidic deposition at a rate faster than they can be replenished by the slow mineral weathering or deposition of nutrient cations from the atmosphere.

2.5.3 Accumulation of sulphur and nitrogen

Acidic deposition results in the accumulation of sulphur and nitrogen in forest soils (Driscoll et al., 2001). As sulphate is released from the soil in response to decreases in the deposition of sulphur, it continues to acidify adjacent streams and lakes. The recovery of surface waters in response to emission controls has therefore been delayed and will not be complete until the sulphur left by a long legacy of acidic deposition is released from soil (Likens et al., 2002).

Observations of declining base saturation in soils and declining calcium (Ca) in streamwater have contributed to concerns that prolonged exposure to acid rain threatens forest health and productivity. According to Hamburg, et al. (2003), prolonged exposure to acid rain, along with a decline in calcium (Ca) in precipitation (Hedin, et al., 1994), is thought to have decreased the availability of base cations in forest soils (Johnson et al. 1994; Lawrence et al. 1999; Huntington, 2000).

Decreasing soil water Ca^{2+} was revealed to have been responsible for reduction in dissolved organic carbon (DOC) adsorption in mineral soils; and this was postulated as a major implication for long-term DOC trends in an upland forested catchment in southern Ontario. Similarly, increased concentrations of DOC in surface waters were also reported in central Europe (Hruška et al., 2009). Declining atmospheric $SO4^{2-}$ deposition has recently been proposed as a unifying driver of widespread DOC trends and the “acid deposition hypothesis” is frequently cited as an explanation for observed increases in surface water DOC. The link between atmospheric $SO4^{2-}$ deposition and increased DOC in surface waters is thought to involve increases in the solubility of organic matter as a result of declines in soil water acidity and/or ionic strength (I) (Hruška et al., 2009).

2.5.4 Acid rain

Dijkstra et al. (2001) reported that, acid rain still remains an important thread to many ecosystems in the United States. Recent studies reporting changes in forest ecosystems in North America and Europe affected by acid rain highlight the need for a better understanding of forest ecosystem functioning (e.g. Likens et al. 1996, 1998). The acidity of precipitation is caused by a surplus of acid anions, such as sulphate and nitrate. Although the deposition of acid anions has declined both in Europe and North America during the last few decades, so has the deposition of base cations (Hedin et al. 1994). The decline in atmospheric base cations has been attributed to declining point source emissions from fuel combustion and industrial processes as well as declining open-source emissions associated with traffic on unpaved roads and agricultural tillage practices. Atmospheric deposition is an important source of base cations for forests growing under nutrient-poor conditions such as those found on many soils in northern Europe and northeastern United States. Hedin et al. (1994) concluded that the declining trend they observed in atmospheric base cation content may have ecological consequences relevant to these forest ecosystems. Moreover, many temperate forest ecosystems of North America and Europe have shown high losses of base cations in the past, and in particular Ca (Federer et al., 1989; Lawrence *et al*., 1995). Likens et al. (1996, 1998) calculated the Ca budget for a watershed in the Hubbard Brook Experimental Forest (New Hampshire, USA) and demonstrated that large quantities of Ca have been lost from the soil complex during the last few decades. Inputs from atmospheric deposition and mineral weathering were not able to make up for these losses, resulting in a depletion of Ca in the watershed. Long-term depletion of Ca and other nutrients in eastern US forests have been attributed to leaching losses caused by acid deposition (Federer et al., 1989; Lawrence et al., 1995; Likens et al., 1996, 1998).

2.5.5 Reduced atmospheric deposition and soil

Oulehle et al (2005) disclosed that during the 1990s the emissions of SO_2 fell dramatically by about 90% in the Czech Republic; the measured throughfall deposition of sulphur to a spruce forest at Načetín in the Ore Mts. decreased from almost 50 kg ha^{-1} in 1994 to 15 kg ha^{-1} in 2005. The throughfall flux of Ca decreased from 17 kg ha^{-1} in 1994 to 9 kg ha^{-1} in 2005; no change was observed for

Mg. During the second half of the 20th century, elevated inputs of acid deposition have affected natural cycles of many elements, leading to the disruption of numerous natural processes. It was also recorded that in the last 20 years, anthropogenic emissions of SO_2 together with mineral dust and subsequent deposition of H^+, SO_4^{-2}, Ca and Mg to forest ecosystems in Europe and Northern America have decreased substantially (Hedin et al., 1994). The previous high rates of acidic deposition raise questions concerning the time-scale of soil and forest ecosystems recovery. The release of formerly stored SO_4^{-2} from the soil (namely from the O horizon) can markedly delay the recovery of soil solution and streams for decades. The low exchangeable pools of Ca and Mg in soils affected by long-term deposition are sensitive to changes in atmospheric inputs of these elements. This could lead, together with continuous Al stress caused by low soil pH, to worsening Ca and Mg supplies for the tree assimilatory tissues (Alewell et al., 2000).

Several researchers have envisaged that irrespective of the high reduction of S inputs, the N deposition during the last two decades has been more or less constant. However, N deposition is characterized by a distinct year-to-year variation, primarily due to varying climatic conditions, thus complicating the detection of time trends. The artificial inputs of nitrogen highly exceed the natural background in European forests. This leads to nitrogen saturation, in which the availability of inorganic nitrogen is in excess of biological demand so that the ecosystem is unable to retain all incoming nitrogen. One of the effects caused by chronic high N deposition is forest decline and NO_3^- pollution of ground and surface waters (Stoddard, 1994). The nitrate leaching to groundwater is associated with flux of cations, which could leads to serious changes in the soil chemical properties.

2.6 Effects of the base cations (Ca and Mg) deficiency on plants and forests

As one of essential nutrient macro-elements for plant growth, calcium plays very important roles in keeping the plant cell structure, resistance of adversity stresses (such as oxidative, drought, chilling and fungal intrusion) and signal transduction (Chaney et al. 2008; Wu 2003; Buchanan et al. 2002). It had been proved that calcium could increase drought resistance of plants (Hong et al. 1996; Lu et al. 1999; Chen 1998). For increasing plant resistance, calcium occupies an important position in keep of stability and internality of cell membrane, in direct or indirect regulation of various metabolisms (Wu 2003; Buchanan et al. 2002).

Calcium depletion in the soil may affect tree growth directly, simply by becoming deficient for growth. Several investigators report decreased primary production, increased canopy dieback and tree mortality because of Ca deficiencies in the soil for many forests of the northeastern United States (Wilmot et al., 1995, 1996; Likens etal.1996, 1998). The loss of Ca (and other base cations) and the resulting pH decrease in poorly buffered soils may adversely affect N mineralization, and consequently N availability in the soil. It was suggested, based on a regional survey in Norway that the soil pH and the supply of base cations affects plant productivity and community composition mainly via their effects on N supply. Finally, loss of Ca and pH decrease in the soil will increase Al mobilization. Lower Ca and higher Al concentrations in soil solution may inhibit Ca uptake, however there is also the potential for direct toxic effects of inorganic Al (Cronan and Grigal, 1995). Based on the Ca and Al contents measured in sugar maple wood and in the soil, it was concluded that trees were suffering from high Al concentrations in the soil causing a decline of sugar maple trees in Ontario, Canada.

Dijkstra (2001) revealed that Ca appears to play, both directly and indirectly, a key role in controlling the distribution of tree species in nutrient poor temperate forests of North America and Europe.

In the same vein, Armbruster, et al. (2002) revealed that magnesium deficiency of trees has played a prominent role in recent research on forest ecosystem, functioning as influenced by acidic deposition. Symptoms of acute Mg deficiency (yellowing of older needles; intercostal chlorosis in leaves) have been observed in forests in many regions of Europe and North America. The annual requirement of Mg by forest stands for biomass production and canopy leaching is in the range of 3– 30 kg ha^{-1} yr^{-1} (Kaupenjohann, 1997). In most cases, the Mg storage in above-ground biomass exceeds the exchangeable Mg pool in the soil. Given this situation, the input of Mg becomes crucial for the overall cycling of Mg in forest ecosystems.

The major sources of Mg to unfertilized forest soils are from atmospheric deposition and silicate weathering (Feger, 1997). There are two main sources of Mg in the atmosphere: (i) sea salt and (ii) mineral particles originating from soil dust or from mining, combustion and other industrial processes. Decreased emission of these particles due to emission controls has led to steep decline in the atmospheric deposition of Ca and Mg in Europe and North America (Matzner and Meiwes, 1994; Hedin et al., 1994). In long-term ecosystem case studies in Germany, the decreasing input of Mg caused by the decrease of atmospheric deposition has been shown to influence the Mg output fluxes with seepage and runoff as well as the Mg nutrition of trees (Alewell et al., 2000; Matzner, 1989), suggesting a strong influence of Mg deposition on the Mg cycle in forest ecosystems. The Mg input by silicate weathering should depend on the mineral composition of the soil and is not easily measured under field conditions (van der Salem, 1999). Mg inputs by weathering in an acid forest soil on sandstone were estimated at about 4 kg ha^{-1} yr^{-1} (Wesselink et al., 1994) and about 0.4 kg ha^{-1} yr^{-1} in an acid forest soil on extremely Mg-poor granite (Stahr et al., 1998).

In a study on the biogeochemistry of base cations in two forest catchments with contrasting lithology in the Slavkov Forest, Czech Republic, Krám et al (1997) added that the symptoms of yellowing of older needles and canopy thinning of old spruce stands may be linked with the unusually low Mg content of foliage and high Al content in the soil solutions, and fine roots. The spruce forest at Lysina showed typical symptoms of decline by needle yellowing attributed to Mg deficiency (Moravčík1995). Foliar chlorosis can be attributed to excessive removal of Mg from older needles to supply new needles. The chlorosis of foliage at Lysina might be characterized as “Type 1 Norway spruce decline” which is caused by Mg deficiency and possibly Ca and Zn deficiency.

2.7 Environmental factor / health implications

Compared to conifers, broadleaf forests are less prone to soil and water acidification, because (1) they often have soils with larger exchangeable base cation pools, (2) the pollution scavenging capacity of deciduous trees is lower, and (3) they grow more slowly and are often less intensively managed. Since the 1980s, atmospheric deposition of acidity has strongly decreased in forest ecosystems, so that the present acidification status of broadleaf forests should be improving**.** Since the 1980s, deposition rates of sulphur on terrestrial ecosystems have strongly decreased in Europe and in North America (Likens et al., 2001). Nitrate and ammonium deposition has either remained stable or has declined. As a consequence, atmospheric deposition of acid has strongly decreased in forest ecosystems. However, deposition of base cation has also decreased (Likens et al., 1996). Consequently, soil and stream water acidification recovery has been slow or has not yet been observed at many monitoring sites. Some studies have even reported an on-going acidification (Watmough and Dillon, 2003).

Forests contribute to soil and surface water acidification in areas of high acid deposition due to the enhanced canopy capture of atmospheric pollutants (‘the scavenging effect’) (Nisbet et al., 1995) especially by dry and mist deposition, as a result of increased turbulent air mixing (Fowler et al., 1989). Another factor is the accumulation and removal of base cations in harvested trees. Compared to conifer, broadleaved forests are less prone to soil and water acidification because (1) they often have soils with larger exchangeable base cation pools (Fichter et al., 1998; Augusto et al., 2002; Mareschal et al., 2010), (2) the pollution scavenging capacity of deciduous trees is lower (De Schrijver et al., 2007; Berger et al., 2009).

2.8 The chemical weathering

Chemical weathering is an important biogeochemical process in the functioning of soils and the ecosystems they support. Acidity is buffered and mineral nutrients are released from the mineral components of the soil into bio-available forms, parts of which are lost from the soil through leaching and biomass harvesting. During the weathering process the proportion of the more easily weathered primary silicate minerals (e.g. feldspars, hornblende, micas) declines while that of the more resistant minerals (e.g. quartz) increases and secondary minerals (e.g. hydrous aluminosilicates) are formed.

The degree of chemical weathering can be measured as the loss of minerals or elements from the upper soil horizon(s). Provided the soil has developed from C-horizon material (uniformity of soil parent material), the loss of minerals or elements from the soil due to weathering can be calculated by comparing the ratio of the content of an easily weatherable mineral or element to that of a conservative mineral or element in the soil to the ratio in the C horizon material. The greater the difference in elemental or mineral ratios between the upper soil and the underlying parent material (C-horizon), the farther the weathering process has proceeded.

As the fraction of more easily weathered minerals declines over time, the rate of weathering can be expected to decline. This implies that the fertility, supply of mineral nutrients and acid buffering capacity of a soil are finite and related to landscape forming processes and geological time scales. Chemical weathering rates determined by mineral dissolution experiments in the laboratory only give short-term values that are often orders of magnitude greater than natural, field based estimates. Depending on the method, field based estimates reflect either current environmental weathering rates (catchment runoff mass balance based values) or long-term average values (soil elemental depletion methods). Estimates of chemical weathering rates in natural weathering environments as a function of time are less easily come by, but one approach that enables this is that of the chronosequence (White et al. 1995).

Trees may directly affect the exchangeable Ca pool in surface soils through their influence on chemical weathering. Several authors have reported apparent differences in mineral weathering caused by different tree species (Augusto et al. 2000; Bergkvist and Folkeson 1995; Bouabid et al. 1995; Quideau et al. 1996; Spyridakis et al. 1967; Tice et al. 1996). Species-induced weathering has been related to the production of organic acids in the soil and the ability of these acids to complex metals or affects soil pH (Antweiler and Drever 1983; Kodama et al. 1983; Lundström and Öhman 1990; Raulund-Rasmussen et al. 1998; Tan 1980; Van Hees and Lundström 1998). Other scientists have argued that exudates by roots or ectomycorhizal fungi promote mineral weathering in the rhizosphere (Gobran et al. 1998; Ochs et al, 1993; van Breemen et al, 2000). Trees may also increase soil weathering rates by modifying the soil pH through CO_2 production (Cawley et al. 1969), by net cation uptake from the soil, or by enhancing deposition of atmospheric acids (Bergkvist and Folkeson 1995; Fölster 1985). We predict that tree species grown on soils poor in base cations and that are able to lower soil pH through mechanisms mentioned above and/or are associated with ectomycorhizal fungi, have a larger impact on the Ca weathering rate in the soil than tree species that do not have these characteristics.

However, the annual supply of Ca for plant uptake through soil weathering in these acidic soils derived from granitic material appears to be very low for all tree species. The role of soil organic acids in mineral weathering processes is still controversial. Other studies have also suggested that organic acids have no large effect on the dissolution rates of primary Ca minerals of granitic rocks, but may be more effective on more mafic rock types (Drever and Vance 1994; Raulund-Rasmussen et al. 1998).

2.8.1 Chemical gradients in regolith formation

Weathering processes transform hard fresh rock into friable weathered rock, which is then physically disrupted to become soil. These regolith materials mantle the land masses and support terrestrial life but their formation involves some of the least understood of Earth's surficial processes. Unweathered granitic plutons are commonly fractured. The fractures are the result of stresses on the rock mass, including those associated with thermal, tectonic, and erosional unloading processes. In unweathered bedrock, the joint fractures are empty planar voids that range in width from a fraction of a millimeter to more than a centimetre (Bergbauer and Martel, 1999). Water flowing down joint fractures initially enters the bedrock mass through inherent microfractures, thereby beginning the chemical weathering process (Meunier et al., 2007). In biotite-bearing granites, ion exchange weathering is an important first step in generating bulk rock porosity. The replacement of interlayer K by hydrated Mg cations results in expansion of the biotite structure as the mineral is transformed to vermiculite (Isherwood and Street, 1976). A smaller expansion of biotite has been noted to occur upon oxidation of the Fe within its structure. In either case, the rock matrix loses much of its mechanical strength and is transformed into a regolith material referred to as *saprock* (Arel and Önalp, 2004). The mesofracture network in saprock opens up the rock mass to extensive percolation of water and vastly increases the surface area for weathering. At this point, hydrolysis becomes an effective weathering process, attacking feldspars and other weatherable minerals. The highly weathered bedrock mass, termed *saprolite* still retains rock texture but most weatherable minerals, such as feldspars, micas, and amphiboles, are altered to clay minerals. Terrestrial plants require a porous substrate in order for their roots to gain structural support and to access water and nutrients. The roots transfer water and nutrients to the above-ground part of the ecosystem and return photosynthetically fixed atmospheric carbon to the belowground part of the ecosystem in the form of root biomass. The roots provide energy to a multitude of soil organisms, promote further weathering, and physically alter regolith morphology (Frazier,et al. 2002).

Sequel to the above notes, chemical gradients in regolith formation can be revealed as the description of the geochemical processes involving the weathered rock material overlying pristine bedrock, as documented by chemical gradients at the pedon scale; the flux of materials are then described through the Critical Zone (CZ). Chemical profiles in the regolith are the record of the CZ written at the pedon scale in the language of geochemistry which are similar to the concentration–depth profiles of marine sediments in that biological, chemical, and physical factors are all of critical important (Brantley, et al., 2007). According to White (1995), the regolith profiles can sometimes be conceptualized as one-dimensional columns characterized by downward water flow and upward solid flow through the weathering engine(Fig.4

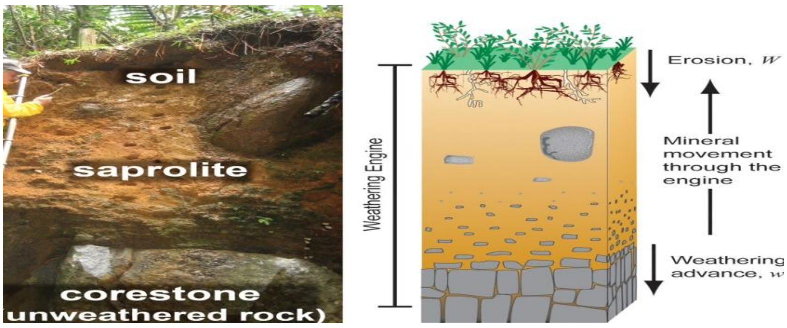


Fig.4: Weathering Engine
Source*: Brantley, et al., (2007).Crossing Disciplines and Scales to understand the Critical Zone. Elements,3; 308.*

2.8.2 Brief biogeochemical description of elements under the study

The alkaline earth metals:

Calcium (Ca) has six naturally occurring isotopes with mass numbers (and percentage abundances) 40 (96.941%), 42 (0.647%), 43 (0.135%), 44 (2.086%), 46 (0.004%) and 48 (0.187%). It is one percent by weight of soils and is generally available but may be lower as it is soluble and can be leached. Ca is the most common of the alkaline earth elements in the Earth's crust (Wedepohl 1995). Common Ca bearing minerals include clinopyroxene, plagioclase, heulandite, stilbite, laumonite, prehnite, tremolite, actinolite, hornblende, epidote, zoisite, grossularite, andradite, calcite, dolomite, gypsum, apatite and sphene (Navrátil, 2003).

Magnesium (Mg) is concentrated in the Earth's mantle, while in the Earth's crust it is most abundant in the oceanic crust and the lower continental crust. Magnesium is central to chlorophyll and aids in the uptake of phosphorus. The minimum amount of magnesium required for plant health is not sufficient for the health of forage animals. A common mineral source of magnesium is the black mica mineral, biotite. Magnesium is generally available in soil, but is missing from some due to leaching by heavy precipitation. It has three naturally occurring isotopes with mass numbers (and percentage abundances) 24 (78.99%), 25 (10.00%) and 26 (11.01%). Magnesium is a major element in most (especially mafic) rock systems and is a major constituent of many rock-forming minerals, where it is typically bound in 6 - fold coordination. The main Mg bearing minerals are olivine, orthopyroxene, clinopyroxene, serpentine, talc, brucite, chlorite, pyrope, amphiboles, biotite, tourmaline, magnesite and spinel. Typical Mg contents of granites are between 160 - 480 meq.kg^{-1}. During the weathering of rocks Mg readily dissolves in weathering solutions and enters the hydrosphere. Magnesium is removed from ocean water by carbonate precipitation or via alteration of oceanic crust, but even so Mg is a conservative element in the seawater (Navrátil, 2003).

The chemical properties of strontium (Sr) closely follow calcium. Strontium can substitute for $Ca^{2+}$and K^+ in feldspars. Strontium forms the minerals celestite ($SrSO_4$) and strontianite ($SrCO_3$). Strontium has four naturally occurring stable isotopes with mass numbers (and percentage abundances) 84 (0.56%), 86 (9.86%), 87 (7.00%) and 88 (82.58%). Plant Sr and Ca can come either from relatively deep in soils through the slow chemical weathering of local substrates or from shallow soil depths by the alteration of silt-sized, carbonate-rich dust. Although Sr is not itself a plant essential nutrient, it is a common chemical tracer of plant-essential nutrient Ca and exists in all common minerals where Ca is present.

Metallic barium (Ba) does not occur in nature, due to its reactivity. The most important naturally occurring minerals are barite ($BaSO_4$) and witherite ($BaCO_3$). However barium usually does not form minerals of its own in igneous rocks. It is usually distributed as a trace constituent among the silicate minerals, especially potassium feldspars and micas, where it substitutes for potassium (Wedepohl 1969). Barium may substitute for large ions such as Pb^{2+} and Sr^{2+}. It may also substitute for Ca, usually in plagioclases, pyroxenes and amphiboles. Barium has seven stable naturally occurring isotopes with mass numbers. With respect to the divalent cations, Ba^{2+} has the largest ionic radius except for Ra^{2+}. It ranks 14th among the elements in the order of abundance in Earth's crust. In terms of overall geochemical behavior Ba most closely follows Sr and Ca. Alkali rocks are usually highly enriched in barium. Granitic rocks with low Ca content (granites, quartzmonzonites) show extremely variable Ba values. Experimental weathering of K feldspar in distilled water showed that Ba is preferentially released from the silicate structure into a solution (Puchelt, 1967).

Table 1: Abundance of the II.A group elements in the Earth's sphere, (all data in meq.kg^{-1} or meq.L^{-1})

Element	Continentl Crust	Abundance in granitic rocks high in Ca	Abundance in granitic rocks low in Ca	Seawater	Abundance in plants(d.m)	Abundance in soils on granites
Ca	1921	2320	788	20	225	435
Mg	1810	1794	132	107	58	595
Sr	7.6	18.3	6.9	0.2	0.5	4.2
Ba	8.5	9.5	12.1	8.7 E-05	0.4	11.5

Source: NAVRÁTIL (2003).

The metals:

Nickel (Ni)

The occurrence of nickel (Ni) is clearly connected with alkaline magma rock as well as sedimentary rocks. Nickel most often accompanies rock-formative magnesium-iron silicates. Due to its sulfophillic tendency, it combines with arsenic and sulphur to form various minerals of its own. In the course of weathering processes, nickel easily undergoes activation, and in the cationic form of Ni^{2+} it can migrate together with its solutions over great distance. Often, however, it is quickly combined with iron and manganese hydroxides (Adriano, 2001).

Chromium (Cr)

Chromium is a metal that rarely occurs in nature. The main mineral containing this element is chromate $FeCr_2O_4$ which contains up to 70% of pure Cr_2O_3. Chromium's higher content in the environment is typically caused by human activities. The risk of global pollution of the natural environment by chromium does not yet exist, although its local emissions into the atmosphere, water and soils may cause its excessive inclusion in biochemical circulation, thus posing a danger to man and animals. Chromium (in small quantities) is an element significant to the life of plants and animals but harmful in large concentrations. Chromium with an oxidation number of six (hexavalent) is more dangerous to living organisms that trivalent chromium, due to its greater ability to diffuse through cell tissue (Barałkiewicz and Siepak, 1999).

Iron (Fe)

Iron is the second most abundant metal and fourth most abundant element in the Earth's crust. Fe is an essential element for almost all living species. In natural conditions, iron primarily comes from the products of weathered rocks and soils around watersheds, controlled by many factors, such as geological processes, soil composition, environmental temperature, precipitation and hydrology. Another important contributor is air deposition (Xing et al, 2011).

Aluminium (Al)

Aluminium is one of the most abundant metallic elements in the Earth's crust, so these pools largely occur as minerals and free Al fractions in soil. Soil Al fractions include exchangeable Al (KCI-extractable), organic Al (pyrophosphate-extractable), amorphous Al (oxalate-extractable) and crystalline Al (citrate- dithionate-bicarbonate extractable). Aluminium is not a plant nutrient and therefore the rate of Al assimilation and cycling by vegetation is low. Conclusively, the higher the charge, the more toxic the species. Al is characterized by mobilization from soil pools to drainage water. Drainage transport of Al occurs in three fractions: particulate Al, organic monomeric Al (organic complexes of Al) and inorganic monomeric Al (inorganic complexes of Al including aquo Al, OH^-, F^- and SO_4^{2-} complexes). The speciation of dissolved Al is particularly significant because inorganic forms of Al are thought to be toxic to plants and aquatic organisms, while organic and particulate Al are not considered toxic (Parker et al. 1989).

Lithium (Li)

Lithium (Li) with atomic number 3 - is a soft, low melting, highly reactive and quickly corroding light metal that heads the family of the alkali metals. Li is a Block S, Group 1, Period 2 element with an atomic weight of 6.94. The number of electrons in each of lithium's shells is [2, 1]. Lithium is a member of the alkali group of metals. Being an alkali metal, lithium is a soft, flammable, and highly reactive metal that tends to form hydroxides. It also has a pretty low density. When Li is in standard conditions, it is the least dense solid element. Lithium is the only alkali metal that does not form the anion, Li^-, in solution or in the solid state. Lithium is a rare element found primarily in molten rock and saltwater in very small amounts. It is understood to be non-vital in human biological processes, although it is used in many drug treatments due to its positive effects on the human brain. Biologically, the widespread occurrence of Li in plants results in a wide, although low-level, distribution of lithium in animals. It is found in trace amount in numerous plants, plankton, and invertebrates, at concentrations of 69 to 5,760 parts per billion (ppb) (Lenntech, 1998).

Potassium (K)

The amount of potassium in a soil may be as much as 80,000 ppm, of which only 150 ppm or 2 percent is available for plant growth. Common mineral sources of potassium are the mica biotite and potassium feldspar, $KAlSi_3O_8$. When solubilised, half will be held as exchangeable cations on clay while the other half is in the soil water solution. Potassium fixation occurs when soils dry and the potassium is bonded between layers of clay. Under certain conditions, dependent on the soil texture, intensity of drying, and initial amount of exchangeable potassium, the fixed percentage may be as much as 90 percent within ten minutes. Potassium may be leached from soils low in clay. Soils with high content of 2:1 clay minerals (micas, vermiculite and high-layer-charge smectite) contain larger amounts of non-exchangeable K than those with kaolinite and other siliceous minerals (Sharply, 1989; Ghosh and Singh, 2001).

Sodium (Na)

Chemical element, symbol: Na, atomic number: 11 and atomic weight 22.9898. It's a soft metal, reactive and with a low melting point, with a relative density of 0.97 at 20ºC (68ºF). From the commercial point of view, sodium is the most important of all the alkaline metals. Sodium is the sixth most abundant element in the Earth's crust, which contains 2.83% of sodium in all its forms. Sodium is, after chlorine, the second most abundant element dissolved in seawater. The most important sodium salts found in nature are sodium chloride (halite or rock salt), sodium carbonate (trona or soda), sodium borate (borax), sodium nitrate and sodium sulphate. Sodium in its metallic form is very important in making esters and in the manufacture of organic compounds. Sodium is also a component of sodium chloride (NaCl) a very important compound found everywhere in the living environment. Sodium reacts quickly with water, and also with snow and ice, to produce sodium hydroxide and hydrogen(Lenntech,1998).

2.9 Base Cations (Ca and Mg): Sources and biogeochemistry at Lysina

Atmospheric deposition and mineral weathering are the principal sources of soluble base cations in forest ecosystems, and these inputs are critical in regulating the acid-base status of forest soils and soil solutions (van Breemen, et al. 1984). Losses of base cations occur largely by drainage outflow or, in managed ecosystems, by biomass removal. Internal processes such as vegetation uptake and release, mineralization of soil organic matter, secondary mineral formation, and cation exchange, all influence the distribution of base cations in the ecosystem, as well as biological availability. The biogeochemistry of Ca, Mg, K, and Na were investigated in a forested catchments in the Czech Republic, underlain by leucogranite, Krám et al (1997) who reported that there is considerable interest in the biogeochemistry of areas underlain by granite and granite-derived rocks because their typically low weathering rates result in high vulnerability to acidic atmospheric deposition.

The granitic site at Lysina showed low concentrations of base cations on the soil exchange complex and in streamwater. Soil and drainage water at Lysina were highly impacted by acidic deposition. Soil pH was extremely acidic (<4.5) throughout the soil profile, and the base saturation of the mineral soil was very low (<5%). Supplies of base cations from atmospheric deposition and soil processes were less than inputs of SO_2^{-4} on an equivalence basis, resulting in low pH and high concentrations of total Al in drainage water. Needle yellowing in Norway spruce was possibly the result of Mg deficiency at Lysina. Catchments on geochemically contrasting rocks serve as valuable end-members of ecosystem sensitivity to elevated levels of acidic deposition because of their extremely distinct content of Ca and Mg (Krám et al. 1997). The cycling of the base cations (Ca, Mg, K, Na) is important to the biogeochemistry of forest ecosystems; Ca, Mg, and K are essential nutrients for plant growth, and low supply rates may affect forest productivity (Federer et al. 1989; Likens & Bormann 1995, Krám et al., 1997).

Krám et al., (1997) concluded that:

“Soils developed in the slow weathering granite catchment showed small pools of exchangeable basic cations, and low soil, soil solution, and stream pH. Weathering and exchange processes at Lysina were unable to neutralize the high inputs of atmospheric acidity, resulting in elevated stream H+ and AlT concentrations. Visible symptoms of forest decline by needle yellowing were probably caused by Mg deficiency at Lysina.”

2.9.1 Mineralization:

The immediate availability of calcium (Ca) in forest ecosystems is largely dependent on mineralization of Ca in organic form, which may differ significantly among tree species. The importance of Ca as a nutrient in temperate forests of the north-eastern United States has been well demonstrated by several studies that reported decreased primary production, and increased canopy dieback because of Ca deficiencies (Likens et al. 1996, 1998; Wilmot et al. 1995, 1996). Net Ca mineralization from decomposing litter is one of the highest Ca fluxes within temperate forest ecosystems and determines to a large extent the immediate Ca availability for plant uptake in these systems.

2.10 Biogeochemical processes controlling soil Ca availability

Several mechanisms control soil Ca availability. Some of these mechanisms are closely linked to tree-growth while others are more related to abiotic factors (climate, soil parent material, relief), while often there is an interaction of both biotic and abiotic factors. These also control the available Ca in the nutrient-poor soil (Dijkstra, F.A., 2003).

- *Atmospheric deposition*: As discussed earlier, atmospheric deposition is an important source of Ca for forests growing on nutrient-poor soils. There is no direct evidence that tree species alter the Ca atmospheric deposition in northeastern U.S. forests.
- *Mineral weathering*: The other important source of Ca is mineral weathering. The rate of Ca mineral weathering depends on abiotic factors like the Ca content and the type of minerals in the soil. However, trees may affect weathering rates by producing organic acids in the soil, thus lowering soil pH and stimulating mineral weathering. Some investigators have reported different weathering rates under different tree species (Bouabid et al. 1995; Tice et al. 1996). Differences in weathering rates beneath different tree species may be mediated by hyphae of ectomycorrhizal fungi that penetrate primary minerals, presumably through the release of organic acids (van Breemen et al. 2000).

- *Calcium biomass storage*: The storage of Ca in the living biomass can vary substantially for different tree species and for species with different age. Johnson and Todd (1990) showed that some tree species showed high losses of exchangeable Ca in the soil due to storage in living biomass.
- *Immobilization in soil organic matter*: The amount of Ca immobilized in soil organic matter can be significantly variable for different tree species. The immobilization of Ca depends on Ca contents of litter and on litterfall and mineralization rates of Ca. The rate of Ca mineralization from decomposing leaf litter is generally closely related to mass loss (Likens et al., 1998). The decomposition rate for leaf litter differs widely for tree species due to differences in litter quality. Tree species with slow litter decomposition rates that build up thicker forest floors (e.g. Finzi et al., 1998*b*) may have higher amounts of Ca immobilized in the forest floor.
- *Vertical movement of exchangeable Ca*: Calcium is lost through leaching with soil water. Leaching losses of cations may vary under different tree species as a result of the release of organic acids and phenolic compounds from litter (Likens et al., 1998). These products may acidify the soil, increasing Al solubility, and ultimately enhancing Ca leaching by the increased Al removing Ca from the binding sites on the exchange complex. Some tree species have deeper root systems than others and may be able to ‘pump’ Ca from deeper soil layers to the soil surface where the Ca eventually will return as leaf litter or with throughfall/stemflow (Dijkstra, et al.2003; Johnson, et al.1985).

2.11 Weathering and atmospheric deposition signatures

Base cation inputs from mineral weathering are often considered to control catchment cation chemistry, as well as providing buffering capacity against acidifying atmospheric deposition (e.g. Hornung et al., 1990). However, atmospheric base cation deposition contributes substantial inputs to UK upland catchments and may significantly influence soil and water chemistry (White et al., 1998; Neal and Kirchner, 2000). Atmospheric seasalt deposition, whilst helping to maintain soil base status in the long-term (White and Cresser, 1995; Farrell, 1995), has also been connected to short-term episodic acidification of streamwaters in Norway, eastern USA and Scotland (Langan, 1989). Such studies have strongly linked temporal trends in deposition chemistry with effects observed in streamwaters. However, there is less consideration of the spatial influence of deposition chemistry on catchment chemistry and particularly on the interplay between weathering and atmospheric sources and the resulting effect on soil base cation compositions and availability.

The ability to accurately quantify chemical weathering in catchment soils is central to the critical load approach which strives to quantify threshold levels of acidifying pollutants above which damage to target environmental systems is predicted to occur (Nilsson and Grennfelt, 1988). Soil mineral weathering, measured in terms of base cation release, is assumed to directly equal the buffering potential of the system. The lack of a standards method for the calculation of weathering rates for both soils and freshwaters compounds the difficulties in applying the critical load methodology. Commonly adopted calculation procedures have been comprehensively reviewed and examples of the lack of agreement between values derived through these methods are given in the literature (Kolka et al., 1996).

The importance of quantifying atmospheric base cations inputs is recognised in critical load investigations. However, there is some debate over the inclusion of atmospheric base cations of both marine and non-marine sources. Marine-derived base cations are not conventionally associated with increases in buffering capacity since their deposition is largely accompanied by the anions Cl^- and SO_4^{2-}, whilst it is generally assumed that all non-marine base cation inputs are associated with inputs of alkaline anions (Draaijers et al., 1997).

3. METHODOLOGY

3.1 Study site/area

Lysina, Slavkov Forest

The study area is located in the petrologically diverse Slavkov Forest (Slavkovskýles), western Bohemia, Czech Republic, about 120 km west of Prague (Fig. 1). The region is preserved as a Protected Landscape Area (CHKO Slavkovskýles). The region was not glaciated and is overlain by residual soil. Streams in the Slavkov Forest experienced marked declines of SO_4^{2}, NO_3^{-}, Ca and Mg concentrations in the 1990s mainly due to decreases in emissions of SO_2 from fossil fuel burning (Shanley et al., 2004) and associated decreases in acidic atmospheric deposition (Hruška and Krám, 2003).

The task in this project involved geochemical studies of base cations, i.e., the concentration analysis of Ca, Mg, and others in a drill core (from a depth of more than 24 meters long) recovered from the naturally base-poor watershed Lysina, in the Slavkov Forest (Fig. 1), located at 50° 03'N and 12° 40'E. The Lysina site is a monolithologic catchment underlain by leucogranite (i.e. acidic igneous rock depleted in Ca and Mg), which is a naturally base-poor bedrock, and therefore the coniferous forest developed at this site is particular vulnerable to effects of the anthropogenic acid deposition and the ongoing export of base cations from the catchment (Krám et al., 2012). The Lysina watershed has elevation which ranges from 829 to 949 meters above sea level, and the site is characterized by mean annual precipitation of about 985 mm. Local vegetation cover consists predominantly (~99%) of Norway spruce (*Picea abies*) plantations, and small occurrences (<1%) of European beech (*Fagus sylvatica).*

3.2 Data Collection and Techniques

Primary sources of geochemical data were collected in this project based on a total of sixty (60) geological (rock/soil) samples which were collected from drill core and soil pit as described below.

3.2.1 Materials and Methods

Drill core:

Drill cores are created using mechanical devices (*appendix iv-v: photographs*). Samples of rocks were collected from these cores. This drill core is 30.3 m deep. The drill core description table and collected geological samples are being labelled: A-D and 1 to 46 for easy identification and valid analyses (*Appendix i).*

Soil Pit:

A soil pit of 150 cm deep was excavated and soil samples were collected from every 15 cm interval (*appendix vi*). Therefore, the soil samples were being collected from ten differentiated zones along the whole pit. A metal metre calibration is used for this measurement while labelled piece of white papers were employed to identify and separate every 15 cm depth. The digging of this soil pit was conceived and developed as to eliminate any possible effects of the drill core operations on the top-most layers of the soil in the study site and to avoid possible surface contamination from drilling devices. The labelling follows in Roman numerals (from I – X). Table is shown in *Appendix ii*.

Laboratory work:

At the Czech Geological Survey (CGS), the samples from cores were cut, homogenized, arranged and labelled for easy identifications (*Appendix vii-photograph*). Thereafter, the samples were being taken to the laboratories for weighing, dissolution, evaporation and digestion processes using the appropriate and standard equipment as described below.

Materials and Laboratory Consumables

For the decomposition of the samples from the drill cores, which include silicate rocks and organic-rich soils, the following materials were used:

Teflon digestion vessels (i.e., 60 mL vessels from Savillex) and commercially available ultra-pure acids (e.g., Rothipuran ultra quality, with metals at ppt levels), and hydrogen peroxide (H_2O_2 solution) to break-down the organics (*for more details on the materials and other laboratory consumables, see the specifications listed in table 3 below*).

Item	**Specification**	**Supplier / part number**	**Number of items**
Teflon vessels	60 ml volume vessels	Savillex / 300-060-03	30 pieces
Teflon closures	for 60 ml vessels	Savillex / 600-058-04	30 pieces
HNO_3 acid	Rothipuran ultra	Roth - R/HN60.3	1 litre bottle
HCl acid	Rothipuran ultra	Roth - R/HN60.4	1 litre bottle
H_2O_2 solution	Rothipuran ultra	Roth - R/HN65.0	0.5 litre bottle
HF acid	Rothipuran ultra	Roth	0.5 litre bottle

Table 3: List of Laboratory materials used for the project

3.2.2 Scientific Methods

Dissolution of Silicates

Silicates are major constituents of rocks and minerals, and strict procedures are employed to digest these silicates from our geological (rock/soil) samples. These silicates are hard and need to be digested through dissolution with strong acids such as nitric acid (HNO_3) and hydrofluoric acid (HF) (see below).

Dissolution of Silicates – Step by Step procedure

- 1.) 100 mg of powdered sample place in Teflon vial
- 2.) Add 1 ml of concentrated HNO_3, and 3ml of concentrated HF
- 3.) Close vial and put on hot plate at 130 ^{0}C for 2-3 days.
- 4.) Open the vial and evaporate to dryness at about 130 ^{0}C
- 5.) Add 1ml of concentrated HNO_3 (1st STEP), keep the vial OPEN, and put on hot-plate.
- 6.) Evaporate to dryness at about 130 ^{0}C
- 7.) Add 1ml of concentrated HNO_3 (2nd STEP), keep the vial OPEN, and put on hot-plate.
- 8.) Evaporate to dryness at about 130 ^{0}C.
- 9.) Add 1ml of concentrated HNO_3 (3rd STEP), keep the vial OPEN, and put on hot-plate.

- 10.) Evaporate to dryness at about 130 ^{0}C.
- 11.) Add 8 ml of concentrated HCL, keep the vial CLOSED and put on hot plate.
- 12.) Leave the vial on hot-plate overnight (ca. 12 hours) at Temp. 70-80^{0}C.
- 13.) A Clean sample solution derived the following morning.
- 14.) Evaporate to dryness at about 130 ^{0}C (keep the vial open).
- 15.) Re-dissolve in 3 ml of concentrated HNO_3 (put on hot-plate overnight).
- 16.) The last stage is placing the sample solution to 100 ml plastic bottles and adding 97 ml of pure H_20 (milliQ). And we have 100 ml sample solution in 3% HNO_3.

3.2.3 Elemental Analysis Method

Basic information on ICP-OES:

It has been 25 years since ICP optical emission spectrometer (ICP-OES) began to be widely used, and is now one of the most versatile methods of inorganic analysis. Its features are often compared to atomic absorption spectrometer. Compared to atomic absorption spectrometer, in which the excitation temperature of air-acetylene flame measures 2000-3000 K, the excitation temperature of argon ICP is 5000 to 7000 K, which efficiently excites many elements.

ICP Optical Emission Spectrometry Principle:

ICP, abbreviation for Inductively Coupled Plasma, is one method of optical emission spectrometry. When plasma energy is given to an analysis sample from outside, the component elements (atoms) are excited. When the excited atoms return to low energy position, emission rays (spectrum rays) are released and the emission rays that correspond to the photon wavelength are measured. The element type is determined based on the position of the photon rays, and the content of each element is determined based on the rays' intensity.

To generate plasma, first, argon gas is supplied to torch coil, and high frequency electric current is applied to the work coil at the tip of the torch tube. Using the electromagnetic field created in the torch tube by the high frequency current, argon gas is ionized and plasma is generated. This plasma has high electron density and temperature (10000 K) and this energy is used in the excitation-emission of the sample. Solution samples are introduced into the plasma in an atomized state through the narrow tube in the centre of the torch tube (Hou, et al., 2000).

Equipment for ICP optical emission spectrometry consists of a light source unit, a spectrometer, a detector and a data processing unit. There are several types of equipment based on differences in the spectrometer and the detector. The most common types are Sequential type and the Simultaneous Type which are shown in (Fig. 5a and b) respectively.

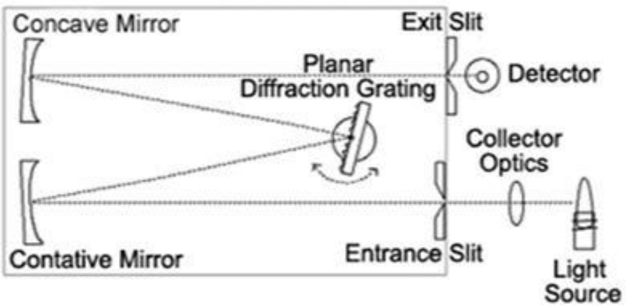


Fig. 5a: ICP-OES Sequential type

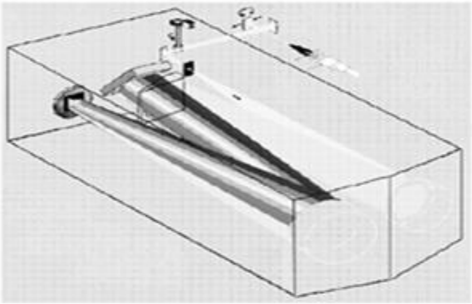


Fig. 5b: ICP-OES Simultaneous

Analytical Chemical Features of ICP-OES:

The following features of ICP-OES distinguish it from atomic absorption spectrometer used for similar purposes.

1. Simultaneous, sequential analysis of multiple elements possible.

2. Wide linear region of analytical curve.

3. Few chemical interference or ionization interference, making analysis of high-matrix-samples possible.

4. High sensitivity (low limit of detection for majority of elements is 10ppb or lower)

5. High number of measurable elements - elements that are difficult to analyze in atomic absorption spectrometry as well as its stability.

Key advantages of ICP-OES:

- Low detection limits.
- Can analyze for many elements at once.
- Fairly simple to run the instrument.
- One disadvantage of ICP-OES is that the instrument is expensive to run (high purity argon gas is required) (Charles, et al., 1997).

ICP-OES Applications:

The concentration of the alkaline earth, alkali and other metal elements namely; Ca, Mg, Ni, Cr, Sr, K, Fe, Al, Ba, Na and Ti were determined by ICP-OES analyzer (720 Series, Agilent Technologies, USA) at CULS Geological Department Laboratory. Calibrations were being performed at the beginning of each analysis with 4 calibration standards prepared by dilution of a stock solution (Analytical CZ9090 MIX010). Simultaneously, signal of three different analytical lines are being collected in order to eliminate spectral interferences and the most sensitive line with best signal/background ratio were being selected to calculate the concentration for the element of interest. It is also of great importance to note that multi-element standard Analytical CZ9090 MIX010 was employed. It has 26 elements in HNO_3 (5% as a matrix). It is a standard ICP for standardization. It is also pertinent to know that for standard concentration elements unit (0.25, 0.5, 1, 10, and 100) were selected to build a calibration curve. The high resolution of the ICP-OES allows the user to choose the desired wavelength, depending on the precision and detection limits required. Good efforts were put in place to ensure that the laboratory analyses results are in line with the universally certified and Internalized Standard Values which shows Mineralogical Composition close to that of the studied Lysina granite (see Table 4.1).

3.2.4 Calculation of Tau-Values from Elemental Concentrations

Normalization Approach:

In order to quantify the dynamics of elemental release and/or accumulation during weathering processes and biological uptake at the study site, it is important to generate '*normalized concentration profiles'* as a function of depth through the regolith formation (i.e., a portion of fractured/weathered rocks that rest on unweathered bedrock). These 'normalized' elemental concentrations, expressed as a parameter (Tau or τ), are being calculated based on the following relationship (Brantley et al., 2007):

$$\tau_{i,m} = \frac{C_{m,w}}{C_{m,p}} \cdot \frac{C_{i,p}}{C_{i,w}} - 1$$

where *C* represents the concentrations of immobile (*i*) or mobile (*m*) elements in weathered (*w*) or parent (*p*) material.

In further explanation of the parameter (*Tau*-τ) used for the calculation:

$C_{m,w}$ = Concentration of mobile elements in the weathered sample;

$C_{m,p}$ = Concentration of mobile elements in parent (unweathered) material/sample;

$C_{i,p}$ = Concentration of immobile elements in the parent rock (unweathered) sample;

$C_{i,w}$ = Concentration of immobile elements (e.g. titanium) in weathered rock sample.

This normalization approach corrects for apparent dilution or enrichment effects that occur when multiple elements react in the rock-soil-water system (Brantley et al., 2007). Commonly, elements such as titanium (Ti) or zirconium (Zr) are used as a reference for the normalization, as these elements are fairly unreactive and thus immobile, during the weathering and soil formation. In this project only the titanium (Ti) is employed for the normalization when calculating the t parameters for our mobile elements of interest (Ca, Mg, Sr, Ba, Ni, Cr, Fe, Al, Li, K and Na).

Accordingly, when $\tau = 0$, the concentration of the element in the weathering profile is identical to that of the unweathered parent (p) material (i.e., in my case this should be the deepest part of the least altered and relatively unweathered bedrock). In contrast, when $\tau <$ or > 0, there is a net loss or gain of the element of interest, respectively. Finally, when $\tau = -1$ there is 100% loss of the element. On the other hand, when $\tau = +1$, there is 100% gain of the element relative to unweathered bedrock.

Using the above normalization approach, one could identify five possible end-member categories of the elemental regolith profiles (Fig. 6), (Brantley et al., 2007), and these include: (1=A) *immobile profiles* with parent-like concentrations at all depths; (2=B) *depletion profiles* with element depletions at the top and gradual increase to parent concentration at the depth; (3=C) *depletion-enrichment profiles* showing also depletion at the top part, but elemental enrichments at a greater depth resulting from mobilization and translocation/precipitation of the element along the weathering profile; (4=D) *additive or enrichment profile*; and finally (5=E) *biogenic profiles* that show typical enrichments at the top and depletion of the concentrations at depth, due to an uptake by a root system.

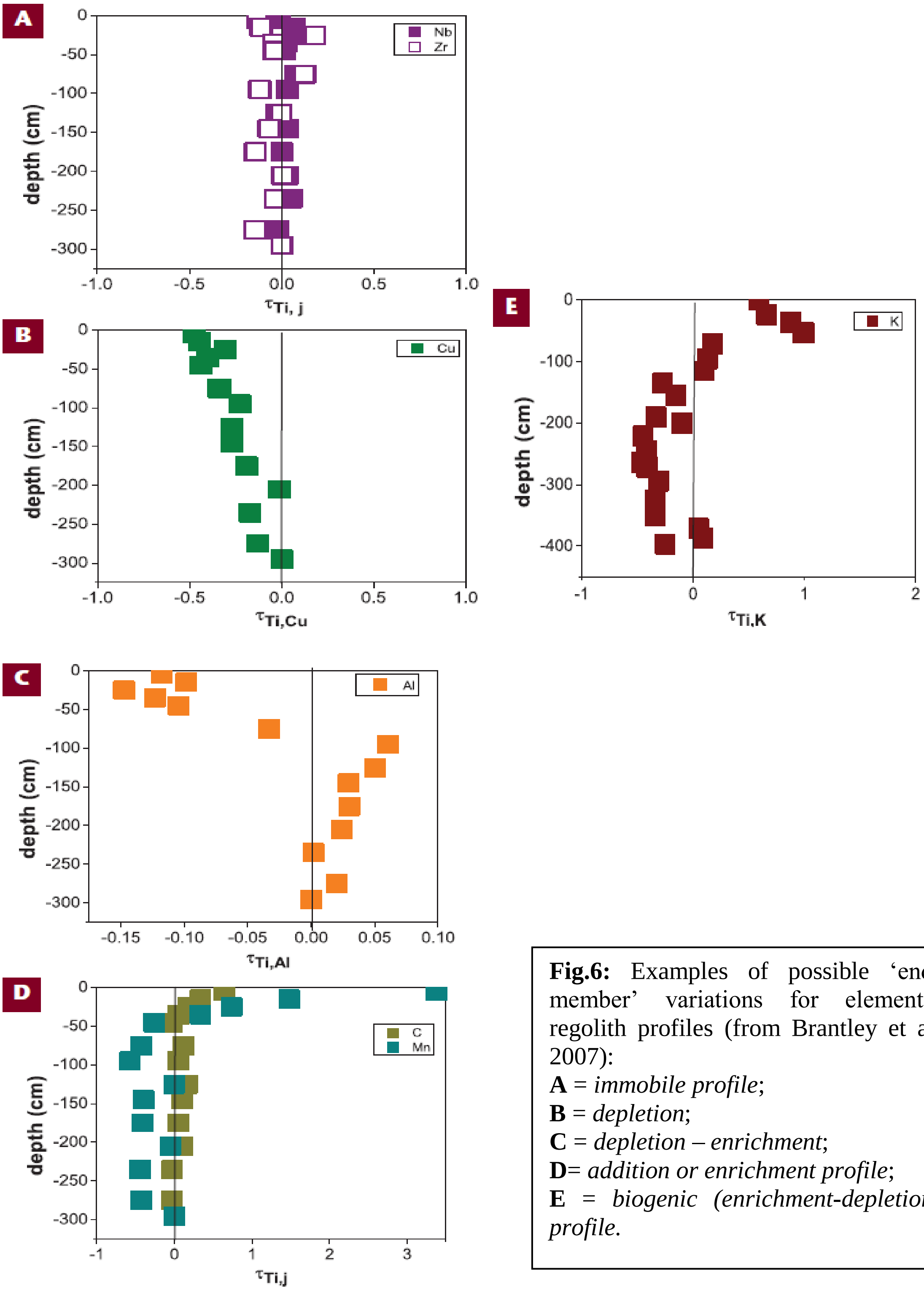


Fig.6: Examples of possible ‘end-member’ variations for elemental regolith profiles (from Brantley et al. 2007):
A = *immobile profile*;
B = *depletion*;
C = *depletion – enrichment*;
D= *addition or enrichment profile*;
E = *biogenic (enrichment-depletion) profile.*

As anticipated, the elemental regolith profiles of Ca, Mg, Sr, Ba, Ni, Cr and others from Lysina exhibit trends with affinities to *depletion*, *biogenic* and *depletion-enrichment profiles*, but only detail analysis of our drill-core concentration data will shade more light on the complex dynamics of biogeochemical cycling and mobility of these elements along the weathering profile.

Overall, 60 bulk samples from the drill core and the pit hole were analyzed for their elemental concentrations, using the state-of-the-art analytical instrumentation that is readily available at KGEV, CZU. Specifically, the concentration of elements (Ca, Mg, Ni, Cr, Sr, Ti and others) were determined by ICP-OES analyzer (720 Series, Agilent Technologies, USA).

Prior to ICP-OES analysis, all samples were being homogenized, weighted and digested in Teflon vials with a mixture of supra-pure hydrofluoric (HF) and nitric acid (HNO_3), (for more details on material specifications see Table 3). Note that the acid digestion steps were being performed in clean and metal-free laboratories located at our partner institution at the Czech Geological Survey, Prague.

The results of the laboratory analysis (as shown in tables 4.2; 4.3) were generated and collected for further computations. For instance, the concentrations in the rock were measured for each of the elements (Ca, Mg, Sr, Ba, Cr, Ni, etc.). This was calculated by multiplying the total amount of each element (in ppm) in the bottle by 100, and next dividing the result by the corresponding weight of each sample element. Therefore, the value of ppm in rock of each sample element is generated. This is the concentration in rock (see table 3). Henceforth, it became easier with subsequent calculation of the Tau (t or τ) values using the formula stated earlier. In the long-run, scientifically quantifiable values were derived.

In conclusion, information in table 4.2 and table 4.3 were used for the plotting of the graphs which describe the elemental regolith profiles of Ca, Mg, Sr, Ba, Ni, Cr, Fe, Al, Li, K and Na.

4. RESULTS

4.1 ICP-OES analyses / method

Our ICP-OES analysed method was validated by analysing two certified rock standards, specifically granite (JG-2) and Serpentinite (UBN).

Results of this validation analysis are briefly presented in Table 4.1. For most of the elements analysed, the certified elemental concentration values agree with our values.

The only inconsistency noticed was the case with alkali earth, Mg in particular. Though, this is not uncommon. It is known with alkali elements because they easily release electrons, thus increasing the electron density in the plasma. If another alkali metal is then introduced into this electron-rich plasma, the free electrons caused a shift of the equilibrium in favour of atoms. Therefore, an apparently higher concentration of an alkali metal is found in the presence of high quantities of another alkali metal when viewing the normal analytic zone (Joachim, 2001).

4.2 Brief description of the key minerals of the granite's drill core thin sections, Lysina- study site:

The thin sections have the components of several minerals and among the major ones include quartz, feldspar (K-feldsper and plagioclase feldspar), micas, and topaz. (see *appendices for more information and miscroscopic imageries).*

Physical/Chemical Composition or Description:

Quartz: This is the dominant element in granitic soil ecosystem. It is composed of silicon dioxide (SiO_2).

K-feldspar: this includes mainly potassium (K), though there is admixture of aluminium and silicon dioxide. It is typically pink or white in colour. [$KAlSi_3O_8$].

Plagioclase feldspar: The plagioclase has sodium-Na, calcium-Ca, silicates and admixtures of barium-Ba, strontium-Sr, lithium-Li, and iron-Fe, as its constituents.

Micas: consist of light and black or dark brown micas. The light type of mica is also referred to muscovite while, the dark type is called biotite. The black mica is also rich in Titanium-Ti.

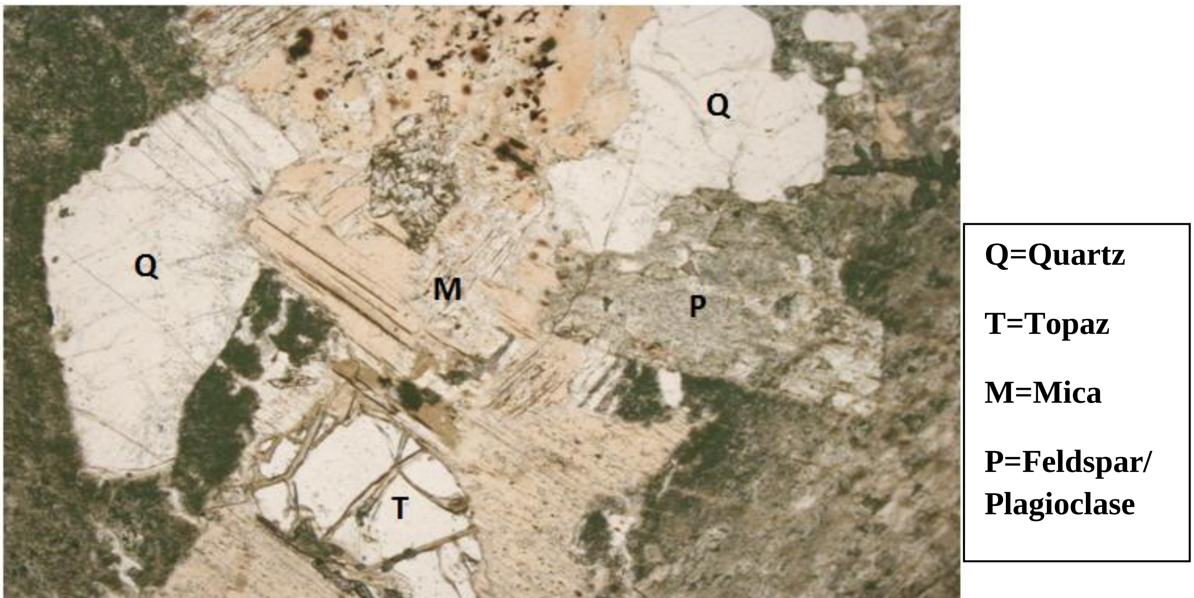
Biotite essentially consists of mainly Magnesium (Mg) with some amount of potassium-K and iron-Fe. [K (Mg, Fe)]. The muscovite mica typically light colour or clear contain Potassium-K, aluminium-Al, silicon oxide-SiO and hydrogen-H. [$KAl_2(AlSi_3)O_{10}(OH)_2$].

Topaz: aluminium-Al, silicon-Si, hydrogen-H, oxygen-O and fluorine-F form the key elements for topaz.[$Al_2(SiO_4)(F,OH)_2$].

DEPTH 30.10m (3010 cm)

QUARTZ	Quartz – forms isolated anhedral grains or their clusters with undulatory extinction, up to 10 vol. %. Usually in spaces between tabular feldspar crystals, it contains often fluid inclusion trails.
FELDSPAR: K-Feldspar Plagioclase Feldspar	Abundant K-Fs (ca 40 vol. %) forms grains up to 3-7 mm, is weakly hazy, ecloses fine grains of sericite and muscovite with disseminated haematite dusting and perthitic exsolutions.
MICA: Biotite Mica Muscovite Mica	Li-mica in less abundant than in previous samples, forms up to 5 vol %, irregular tiny flat crystals, is weakly brownish, Albite – almost clear, without alterations, usually as subhedral flakes with tiny grains of white mica.
TOPAZ	Topaz usually as individual relict grains up to 1 mm surrounded by aggregate of replacing sericite and clay minerals or completely replaced by their mixture.

FIG.9: Microscopic view of minerals in the Lysina granite



Source: **Veronika Štědrá and Tomáš Jarchovský (2014) Oral Conversation, interview and information from the Nikon Eclipse 80i microscopic.**

Table 4.1: Elemental analysis of certified rock standards; granite (JG-2) and serpentinite (UBN)

method 1												
Soln Label	Ca 317.933	Ca 393.366	Ca 315.887	Cr 283.563	Li 670.783	Ni 231.604	Sr 421.552	Ti 334.941	Ti 336.122	Mg 279.553	Mg 280.270	Mg 285.213
granite (JG-2)	4.547	4.556	4.539	0.006	0.040	-0.001	0.015	0.241	0.240	0.221	0.220	0.222
serpenti(UBN)	7.928	8.350	7.899	2.293	0.026	1.849	0.007	0.570	0.568	58.661	94.127	149.614
method 2												
Soln Label	Ca 317.933	Ca 393.366	Ca 315.887	Cr 283.563	Li 670.783	Ni 231.604	Sr 421.552	Ti 334.941	Ti 336.122	Mg 279.553	Mg 280.270	Mg 285.213
granite (JG-2)	4.775	4.722	4.662	0.006	0.054	0.001	0.015	0.241	0.241	0.229	0.226	0.238
serpenti(UBN)	8.310	8.649	8.202	2.285	0.034	1.886	0.007	0.559	0.560	55.407	93.880	141.190
certificate	Ca			Cr	Li	Ni	Sr	Ti		Mg		
granite (JG-2)				0.0045-0.0089	0.0359-0.0439	0.00201-0.0026	0.016-0.01821	0.1798-0.2997		0.241-0.6034		
serpenti(UBN)	8.08-9.00			2.09-2.516	0.0234-0.032	1.740-2.1303	0.0067-0.0118	0.529-0.677		199		

TABLE 4.2: ELEMENTAL CONCENTRATION (IN PPM) IN ROCKS/SOILS AS A FUNCTION OF DEPTH (IN CM)

Sln Label (Sample)	**Depth (cm)**	**Weight(g)**	**Ca(ppm) in Rock**	**Cr(ppm) in Rock**	**Li(ppm) in Rock**	**Ni(ppm) in Rock**	**Sr(ppm) in Rock**	**Ti(ppm) in Rock**	**Mg(ppm) in Rock**	**K(ppm) in Rock**	**Fe(ppm) in Rock**	**Al(ppm) in Rock**	**Ba(ppm) in Rock**	**Na(ppm) in Rock**
I	15	0.20	820.85	11.66	444.29	2.30	16.86	1366.18	622.38	16669.73	5722.42	47841.64	64.66	11976.75
II	30	0.21	630.89	10.70	775.31	1.02	14.57	1702.36	639.92	22231.56	6483.53	62013.00	58.31	15442.67
III	45	0.20	683.70	15.04	727.02	1.85	19.73	1547.78	1049.89	21887.82	11340.46	65620.92	87.54	14423.49
IV	60	0.21	1086.81	19.97	769.85	5.35	21.85	1621.09	1773.57	22386.53	15661.20	72694.59	103.54	14455.84
V	75	0.20	712.46	18.90	614.07	2.34	21.93	1945.63	1282.63	22540.37	14397.25	68469.91	98.69	14797.16
VI	90	0.22	1309.51	12.64	789.77	4.25	17.10	1061.70	1403.77	22315.98	11525.28	65281.38	68.28	14287.76
VII	105	0.20	1681.58	14.76	811.14	5.30	20.31	1167.80	1627.75	25150.71	12102.69	76092.74	84.45	16485.11
VIII	120	0.21	1888.53	16.17	886.91	6.35	21.80	1468.49	1763.53	22647.72	11207.36	71235.14	89.46	14570.65
IX	135	0.21	1363.28	7.91	1055.50	3.77	16.74	1128.04	1298.79	27598.53	8918.04	87816.73	39.92	16843.76
X	150	0.20	1261.43	7.52	990.57	3.14	14.82	1188.52	1144.51	26385.38	8505.46	80690.06	37.27	15934.47
A	15	0.20	838.41	9.53	622.51	2.02	13.98	1020.18	902.84	19751.89	8489.03	58432.45	74.07	12845.07
B	30	0.23	693.67	9.88	776.48	2.21	15.83	1103.61	978.72	21986.98	8214.34	66095.90	75.90	14237.15
C	60	0.21	748.50	11.80	843.50	2.30	20.16	1346.98	1157.79	24688.26	8528.12	74796.57	89.24	16214.40
D	90	0.22	685.63	10.01	873.56	1.98	18.39	1230.48	1085.35	23751.46	8444.22	71505.94	80.84	15385.20
1	115	0.20	2154.22	4.82	1035.24	2.46	16.48	624.95	1356.07	27118.76	9409.02	84262.81	40.46	17887.77
2	160	0.22	1506.08	1.53	939.06	2.08	12.72	497.82	3336.39	25028.62	9536.47	75659.93	47.70	10600.10
3	190	0.22	1749.97	1.54	986.85	2.51	15.02	481.09	4088.97	22730.89	9079.24	73531.26	57.09	8465.82
4	218	0.21	1656.67	0.82	1025.60	1.04	13.26	539.56	1290.17	25038.72	9062.33	70166.15	44.95	15214.41
5	270	0.20	2419.11	1.05	965.15	0.43	11.15	474.03	811.46	27012.09	8369.95	73003.57	30.92	17353.33
6	320	0.20	2159.97	0.85	942.67	0.83	11.32	524.04	953.72	25042.85	8711.57	70608.92	41.57	16226.33
7	370	0.21	2159.02	1.01	935.53	0.17	11.61	373.14	919.91	26032.55	8231.15	70818.65	41.76	16897.35
8	440	0.21	2400.16	0.99	920.90	0.14	9.42	421.57	848.96	27157.36	7914.14	72962.17	21.80	17044.66
9	490	0.24	2107.29	0.58	1066.87	0.86	14.61	488.23	948.79	26269.93	8634.74	69510.15	68.06	15413.19

TABLE 4.2: ELEMENTAL CONCENTRATION (IN PPM) IN ROCKS/SOILS AS A FUNCTION OF DEPTH (IN CM) (continuation page)

10	530	0.20	1885.56	1.08	956.50	0.67	17.05	423.23	926.11	28854.31	7714.30	72191.08	138.64	16502.23
11	595	0.20	2786.37	0.77	1073.53	0.55	10.25	421.18	1113.78	26859.09	8060.87	71154.14	16.75	17747.93
12	645	0.20	2518.85	1.31	1072.90	1.31	9.07	408.09	999.60	24692.57	8381.29	72419.07	16.24	17981.18
13	695	0.20	1660.63	0.65	821.27	0.22	6.00	258.25	518.57	19768.99	6059.45	51336.63	8.39	13131.98
14	740	0.20	2709.21	1.02	1062.70	0.73	9.57	354.77	694.03	24893.81	8002.57	70881.59	18.76	18853.85
15	790	0.21	2525.03	1.62	1262.46	0.97	13.22	429.35	744.73	27431.11	9420.28	72032.85	45.18	18024.53
16	850	0.22	2235.92	0.45	1015.98	0.36	9.29	388.06	594.66	25038.82	6913.29	69681.01	13.49	18646.99
17	890	0.20	2699.31	1.14	1009.30	0.61	9.29	357.41	851.60	25092.32	7203.59	69170.25	10.38	18141.23
18	950	0.20	2783.00	0.49	968.71	0.50	12.81	330.73	904.52	23240.73	6409.47	67773.75	9.83	18028.82
19	995	0.21	3319.33	0.41	955.64	1.12	17.88	334.39	916.06	23947.72	6425.77	69393.97	9.65	17868.33
20	1040	0.20	2564.85	0.80	1007.18	0.37	10.50	356.02	675.78	23984.62	6995.06	68419.14	9.05	18648.37
21	1095	0.20	2724.50	0.26	1107.03	0.94	11.99	372.57	768.81	24712.97	7518.93	67952.96	11.04	17702.95
22	1150	0.20	3497.93	0.81	971.30	0.53	28.51	338.71	883.99	25260.98	7491.49	69082.27	9.59	17704.60
23	1195	0.21	2687.29	0.38	1065.47	0.86	12.59	373.74	697.49	24758.04	7231.19	71035.12	13.24	19090.22
24	1250	0.20	3449.46	0.69	1074.48	1.21	16.26	309.74	836.54	26424.18	6657.96	76276.20	18.06	20002.61
25	1290	0.20	2615.71	0.37	1278.95	0.46	12.78	478.05	1075.90	25382.44	8699.77	70489.73	10.81	17912.88
26	1354	0.20	2914.05	0.14	943.16	-0.09	12.48	318.05	906.79	25303.90	6179.75	69590.60	10.74	17750.76
27	1385	0.21	3036.24	0.63	1039.07	0.46	13.46	336.99	1074.54	25465.63	6587.24	74019.25	9.69	19413.30
28	1440	0.21	5583.21	0.79	1128.83	1.28	35.68	325.92	1169.21	24367.52	7027.32	69915.61	10.81	16792.97
29	1485	0.20	2589.98	0.93	1016.06	0.62	12.43	345.88	709.02	26327.71	6873.85	71054.20	12.89	18328.45
30	1545	0.21	2870.78	-0.12	1156.48	0.93	12.41	358.93	799.37	26492.49	7227.89	73544.02	10.90	18497.21
31	1595	0.23	2691.06	0.52	1254.68	0.18	12.29	445.50	874.52	26211.48	8200.57	69739.14	15.09	16581.62
32	1640	0.20	3245.23	0.36	1256.05	0.90	13.85	298.53	1288.54	28035.65	6587.74	79804.21	16.91	17513.67
33	1690	0.21	3287.31	0.43	1276.07	0.93	17.14	352.97	1329.49	26465.16	7078.57	74452.47	19.70	16733.98
34	1745	0.21	3072.80	0.22	1395.92	1.28	11.72	339.04	1150.99	29087.16	7495.30	78752.71	13.20	17682.06
35	1795	0.20	4323.08	0.63	1601.89	1.88	17.12	269.93	1542.78	32682.79	8920.33	76962.93	8.89	13375.44
36	1855	0.20	6814.46	0.77	1848.57	1.21	10.27	380.03	1344.97	24302.07	10209.49	81253.22	4.22	18034.46

TABLE 4.2: ELEMENTAL CONCENTRATION (IN PPM) IN ROCKS/SOILS AS A FUNCTION OF DEPTH (IN CM) (continuation page)

37	1895	0.21	3938.69	0.40	1221.83	1.65	13.17	304.62	1266.87	16084.96	7385.08	59024.84	3.54	10933.50
38	1940	0.20	3351.98	0.43	1871.80	0.67	11.08	399.56	950.69	18504.21	11752.85	65502.64	4.61	5575.52
39	1990	0.21	11819.31	0.59	1097.14	1.01	12.25	186.13	947.01	18869.99	5916.31	64247.64	4.14	13516.98
40	2055	0.20	3655.90	0.26	1238.70	0.65	10.72	244.04	1612.05	23397.73	6061.28	72070.83	10.24	12157.31
41	2095	0.20	3198.98	0.34	950.35	0.92	8.94	199.95	1513.09	22287.77	4662.16	69476.73	5.03	13095.58
42	2145	0.21	5079.16	0.12	1317.48	0.96	24.42	244.89	566.88	45449.10	6888.79	97124.13	20.98	1956.59
43	2195	0.21	3903.18	0.50	931.35	0.84	11.02	284.69	991.08	25342.14	6089.12	72767.17	9.05	17667.39
44	2245	0.20	5383.43	0.47	717.67	0.63	16.47	180.23	794.76	22964.26	6179.90	64799.55	6.61	14747.99
45	2295	0.21	7260.47	0.30	1633.05	0.70	18.93	472.99	1116.22	27489.78	10987.44	76410.14	9.64	17088.02
46	2345	0.20	4136.83	0.44	1203.76	0.47	14.81	288.25	770.54	25375.75	7693.29	72146.00	10.11	18002.33

TABLE 4.3: CALCULATED TAU-VALUES AS A FUNCTION OF DEPTH USING TITANIUM (Ti) AS REFERENCE

Soln Label (Sample)	Depth(cm)	Weight(g)	Tau (Ca) Ti	Tau (Cr) Ti	Tau (Li) Ti	Tau (Ni) Ti	Tau (Sr) Ti	Tau (Mg) Ti	Tau (K) Ti	Tau (Fe) Ti	Tau (Al) Ti	Tau (Ba) Ti	Tau (Na) Ti
I	15	0.200	-0.964	5.157	-0.911	-0.213	-0.752	-0.848	-0.852	-0.834	-0.850	0.642	-0.840
II	30	0.207	-0.978	3.523	-0.876	-0.722	-0.829	-0.874	-0.842	-0.849	-0.844	0.186	-0.835
III	45	0.202	-0.974	5.992	-0.872	-0.445	-0.745	-0.774	-0.829	-0.710	-0.818	0.958	-0.831
IV	60	0.213	-0.960	7.870	-0.870	0.534	-0.730	-0.635	-0.833	-0.617	-0.808	1.212	-0.838
V	75	0.203	-0.978	6.013	-0.913	-0.438	-0.774	-0.779	-0.859	-0.706	-0.849	0.761	-0.861
VI	90	0.217	-0.927	7.587	-0.796	0.866	-0.677	-0.558	-0.745	-0.569	-0.736	1.231	-0.755
VII	105	0.200	-0.915	8.100	-0.810	1.113	-0.652	-0.534	-0.739	-0.589	-0.721	1.505	-0.743
VIII	120	0.210	-0.924	6.954	-0.834	1.017	-0.702	-0.598	-0.812	-0.697	-0.791	1.116	-0.819
IX	135	0.212	-0.928	4.061	-0.744	0.559	-0.702	-0.615	-0.703	-0.686	-0.665	0.229	-0.728
X	150	0.201	-0.937	3.570	-0.771	0.232	-0.750	-0.677	-0.730	-0.715	-0.708	0.090	-0.756
A	15	0.203	-0.951	5.756	-0.832	-0.073	-0.724	-0.703	-0.764	-0.669	-0.753	1.526	-0.770
B	30	0.229	-0.962	5.492	-0.806	-0.060	-0.711	-0.702	-0.757	-0.703	-0.742	1.398	-0.764
C	60	0.210	-0.967	5.345	-0.828	-0.202	-0.698	-0.711	-0.776	-0.748	-0.761	1.308	-0.780
D	90	0.217	-0.967	4.877	-0.805	-0.249	-0.700	-0.704	-0.765	-0.727	-0.750	1.284	-0.772
1	115	0.201	-0.795	4.577	-0.546	0.840	-0.470	-0.273	-0.472	-0.401	-0.420	1.250	-0.478
2	160	0.215	-0.820	1.219	-0.483	0.944	-0.487	1.244	-0.389	-0.239	-0.347	2.327	-0.612
3	190	0.217	-0.783	1.312	-0.437	1.440	-0.372	1.851	-0.425	-0.249	-0.342	3.129	-0.679
4	218	0.206	-0.817	0.102	-0.478	-0.103	-0.506	-0.198	-0.435	-0.331	-0.440	1.898	-0.485
5	270	0.205	-0.697	0.601	-0.442	-0.579	-0.528	-0.427	-0.308	-0.299	-0.339	1.264	-0.334
6	320	0.201	-0.755	0.172	-0.508	-0.266	-0.567	-0.392	-0.420	-0.341	-0.422	1.750	-0.437
7	370	0.206	-0.656	0.956	-0.314	-0.792	-0.376	-0.175	-0.153	-0.125	-0.185	2.882	-0.176
8	440	0.213	-0.661	0.703	-0.401	-0.841	-0.551	-0.325	-0.217	-0.254	-0.256	0.797	-0.263
9	490	0.242	-0.744	-0.151	-0.402	-0.184	-0.400	-0.351	-0.347	-0.299	-0.389	3.832	-0.426
10	530	0.204	-0.735	0.842	-0.381	-0.260	-0.192	-0.268	-0.172	-0.277	-0.268	10.360	-0.291
11	595	0.200	-0.608	0.323	-0.303	-0.388	-0.513	-0.117	-0.227	-0.242	-0.276	0.377	-0.235

TABLE 4.3: CALCULATED TAU-VALUES AS A FUNCTION OF DEPTH USING TITANIUM (Ti) AS REFERENCE (continuation page)

12	645	0.200	-0.633	1.325	-0.279	0.494	-0.554	-0.180	-0.264	-0.184	-0.237	0.382	-0.197
13	695	0.201	-0.618	0.821	-0.130	-0.611	-0.535	-0.329	-0.071	-0.070	-0.147	0.126	-0.075
14	740	0.200	-0.547	1.071	-0.180	-0.036	-0.459	-0.346	-0.148	-0.105	-0.142	0.834	-0.033
15	790	0.207	-0.651	1.718	-0.196	0.046	-0.384	-0.421	-0.226	-0.131	-0.281	2.643	-0.238
16	850	0.222	-0.658	-0.166	-0.284	-0.571	-0.520	-0.488	-0.217	-0.294	-0.230	0.205	-0.126
17	890	0.200	-0.552	1.293	-0.227	-0.209	-0.479	-0.204	-0.148	-0.201	-0.170	0.007	-0.077
18	950	0.203	-0.500	0.073	-0.197	-0.300	-0.222	-0.084	-0.146	-0.230	-0.119	0.032	-0.007
19	995	0.209	-0.411	-0.128	-0.219	0.556	0.071	-0.085	-0.132	-0.238	-0.110	-0.001	-0.029
20	1040	0.204	-0.573	0.621	-0.226	-0.516	-0.409	-0.366	-0.183	-0.221	-0.176	-0.119	-0.048
21	1095	0.204	-0.566	-0.502	-0.186	0.177	-0.354	-0.310	-0.195	-0.199	-0.217	0.028	-0.135
22	1150	0.201	-0.386	0.729	-0.214	-0.273	0.690	-0.126	-0.094	-0.121	-0.123	-0.017	-0.048
23	1195	0.205	-0.573	-0.262	-0.220	0.074	-0.325	-0.376	-0.196	-0.233	-0.185	0.228	-0.071
24	1250	0.200	-0.343	0.601	-0.056	0.803	0.047	-0.102	0.030	-0.152	0.051	1.010	0.168
25	1290	0.203	-0.674	-0.447	-0.266	-0.554	-0.463	-0.246	-0.354	-0.276	-0.366	-0.214	-0.317
26	1354	0.204	-0.456	-0.684	-0.187	-1.128	-0.212	-0.046	-0.033	-0.228	-0.060	0.172	0.016
27	1385	0.206	-0.465	0.354	-0.156	-0.368	-0.199	0.066	-0.083	-0.225	-0.057	-0.003	0.048
28	1440	0.213	0.013	0.730	-0.056	0.816	1.187	0.195	-0.096	-0.148	-0.083	0.145	-0.066
29	1485	0.205	-0.557	0.941	-0.198	-0.162	-0.281	-0.317	-0.079	-0.214	-0.121	0.289	-0.039
30	1545	0.212	-0.527	-1.248	-0.121	0.207	-0.309	-0.258	-0.108	-0.204	-0.124	0.049	-0.066
31	1595	0.227	-0.641	-0.158	-0.229	-0.815	-0.447	-0.344	-0.286	-0.270	-0.328	0.175	-0.323
32	1640	0.204	-0.356	-0.126	0.150	0.409	-0.071	0.441	0.138	-0.126	0.145	0.961	0.065
33	1690	0.215	-0.448	-0.114	-0.012	0.226	-0.027	0.258	-0.091	-0.205	-0.096	0.933	-0.139
34	1745	0.205	-0.463	-0.542	0.124	0.749	-0.309	0.132	0.039	-0.125	-0.006	0.347	-0.054
35	1795	0.201	-0.050	0.683	0.624	2.236	0.271	0.910	0.469	0.310	0.223	0.141	-0.099
36	1855	0.200	0.067	0.470	0.334	0.483	-0.457	0.186	-0.222	0.068	-0.080	-0.614	-0.135
37	1895	0.206	-0.232	-0.057	0.099	1.523	-0.132	0.392	-0.358	-0.037	-0.168	-0.597	-0.346
38	1940	0.201	-0.503	-0.233	0.280	-0.215	-0.445	-0.206	-0.439	0.165	-0.298	-0.601	-0.747

TABLE 4.3: CALCULATED TAU-VALUES AS A FUNCTION OF DEPTH USING TITANIUM (Ti) AS REFERENCE (continuation page)

39	1990	0.212	2.762	1.281	0.610	1.527	0.317	0.698	0.228	0.258	0.478	-0.230	0.318
40	2055	0.200	-0.109	-0.222	0.392	0.251	-0.117	1.213	0.166	-0.012	0.270	0.458	-0.092
41	2095	0.200	-0.052	0.218	0.299	1.143	-0.105	1.526	0.351	-0.076	0.489	-0.128	0.189
42	2145	0.206	0.229	-0.660	0.469	0.825	0.995	-0.228	1.248	0.114	0.698	1.964	-0.855
43	2195	0.205	-0.186	0.268	-0.104	0.377	-0.224	0.164	0.080	-0.151	0.097	0.102	0.129
44	2245	0.201	0.776	0.872	0.092	0.633	0.835	0.477	0.549	0.363	0.545	0.274	0.491
45	2295	0.211	-0.091	-0.548	-0.057	-0.316	-0.199	-0.213	-0.296	-0.080	-0.308	-0.295	-0.344
46	2345	0.205	-0.149	0.095	0.141	-0.245	0.029	-0.108	0.067	0.057	0.073	0.214	0.134

FIG. 7 *A-D*: ELEMENTAL CONCENTRATION OF ALKALI EARTH METALS IN WEATHERING PROFILE (LYSINA)

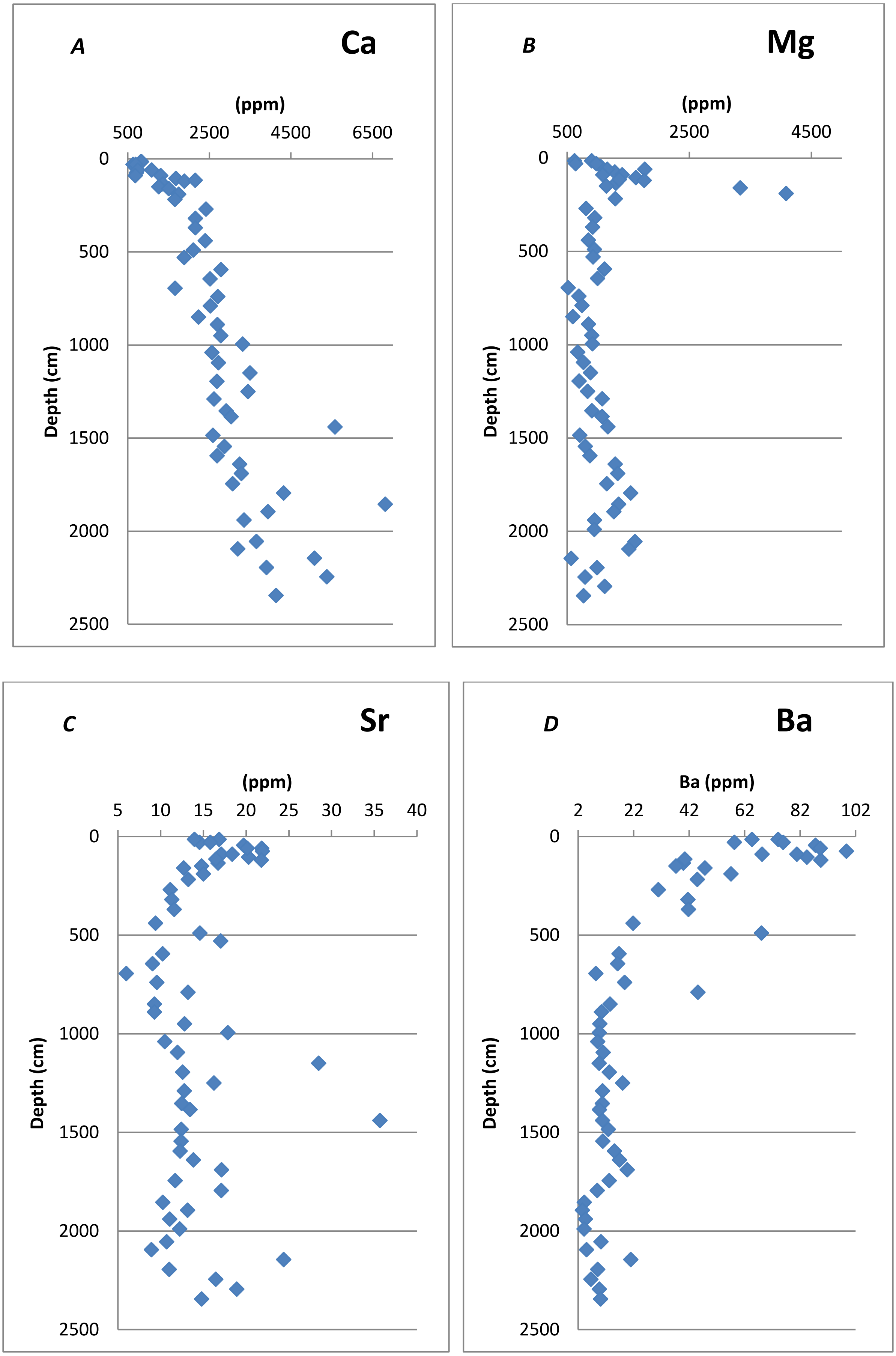
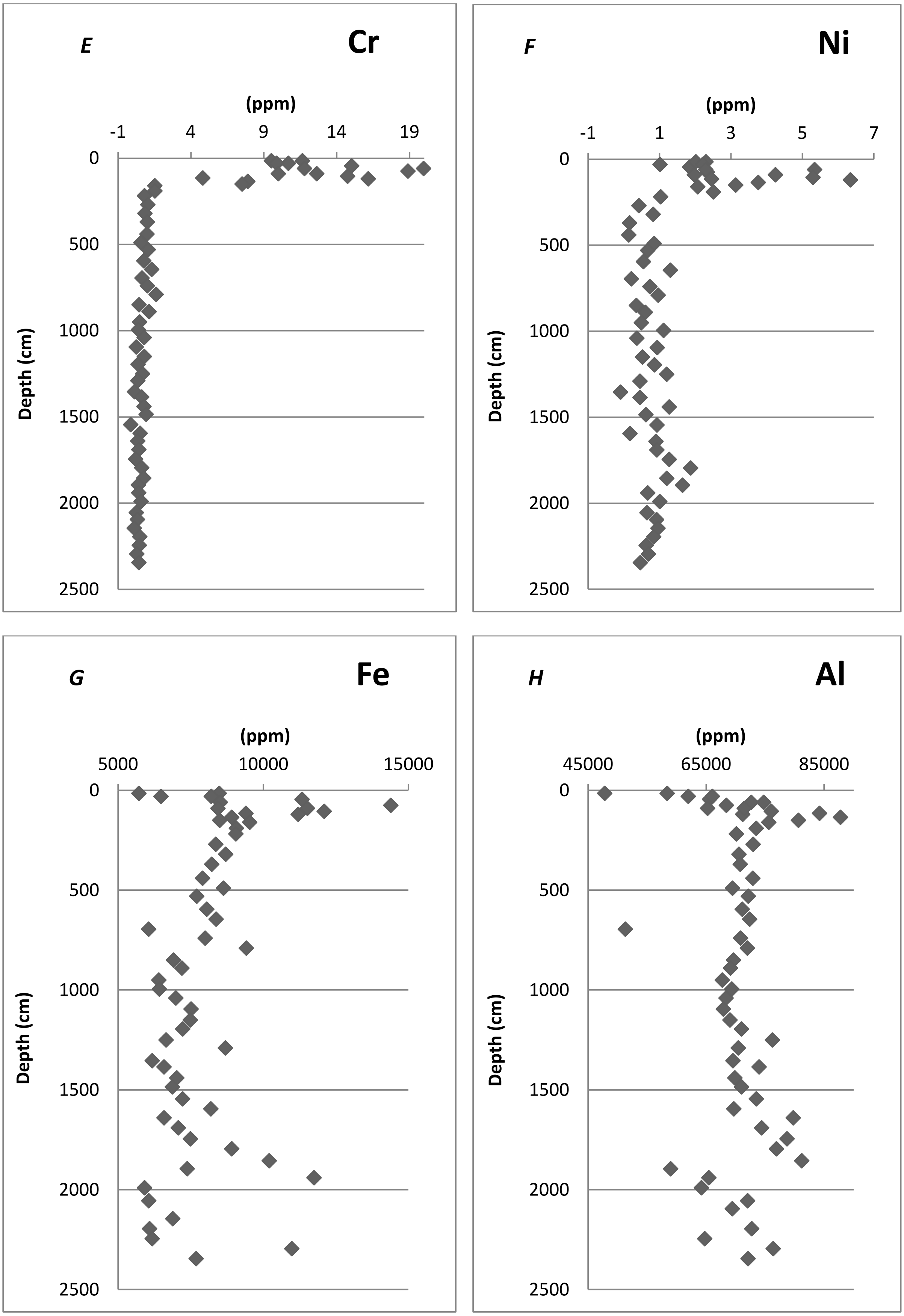
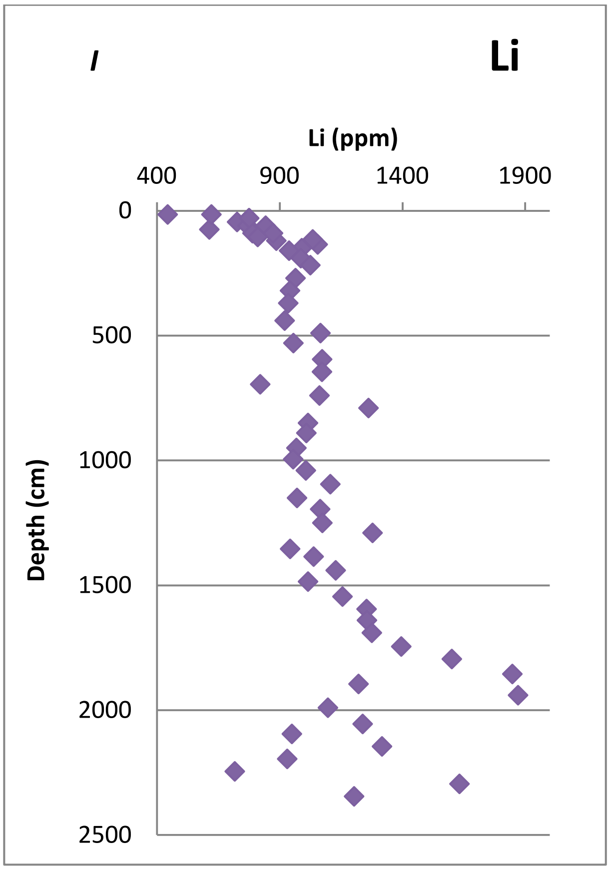
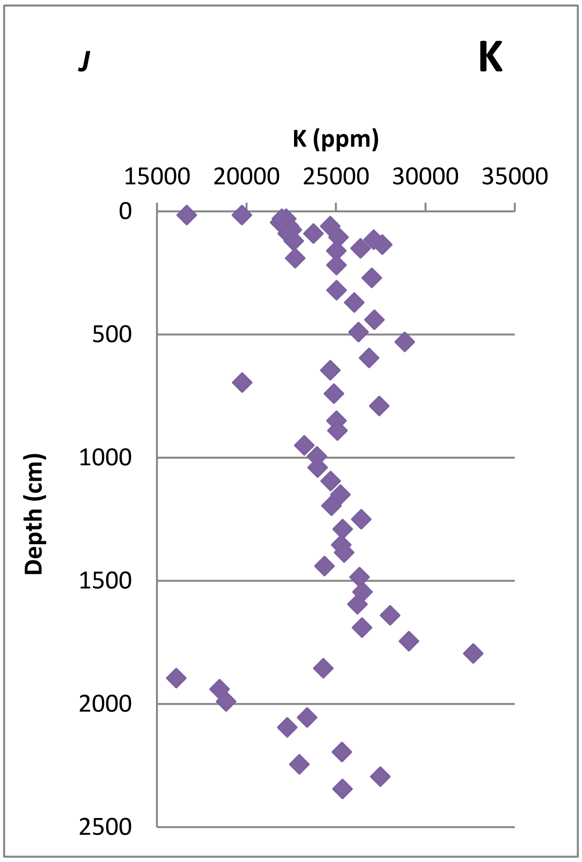


FIG. 7 *E-K* : ELEMENTAL CONCENTRATION OF METALS (Cr, Ni, Fe,) AND OTHER ELEMENTS (Al, Li, K, Na) IN WEATHERING PROFILE (LYSINA)




I
Li
Li (ppm)
400
900
1400
1900
0
500
1000
1500
2000
2500
Depth (cm)


J
K
K (ppm)
15000
20000
25000
30000
35000
0
500
1000
1500
2000
2500
Depth (cm)

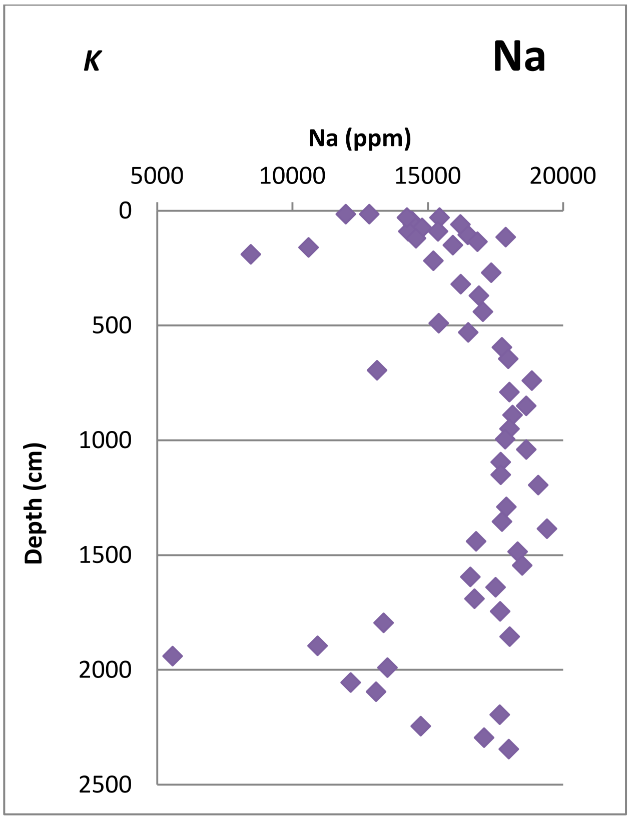
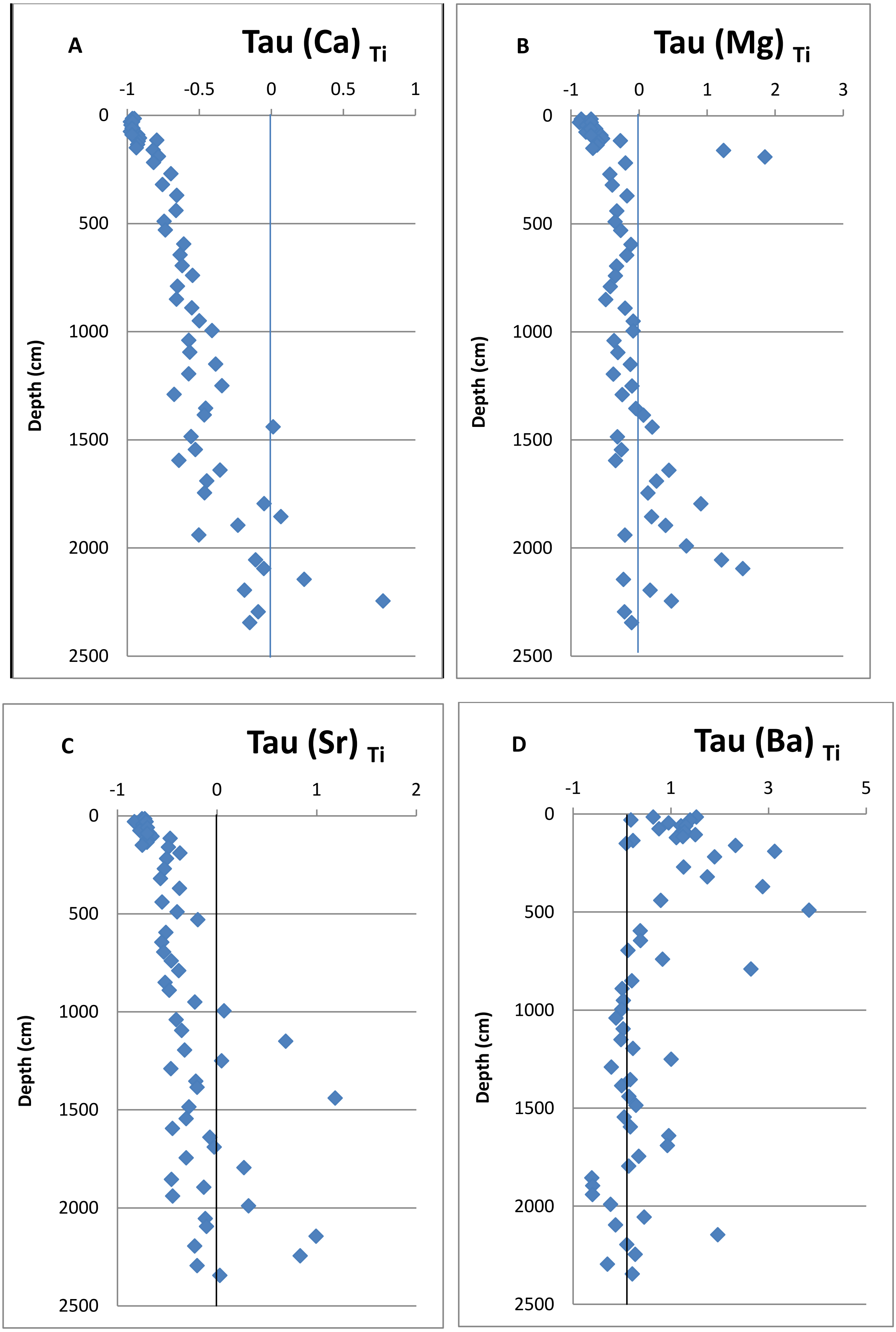
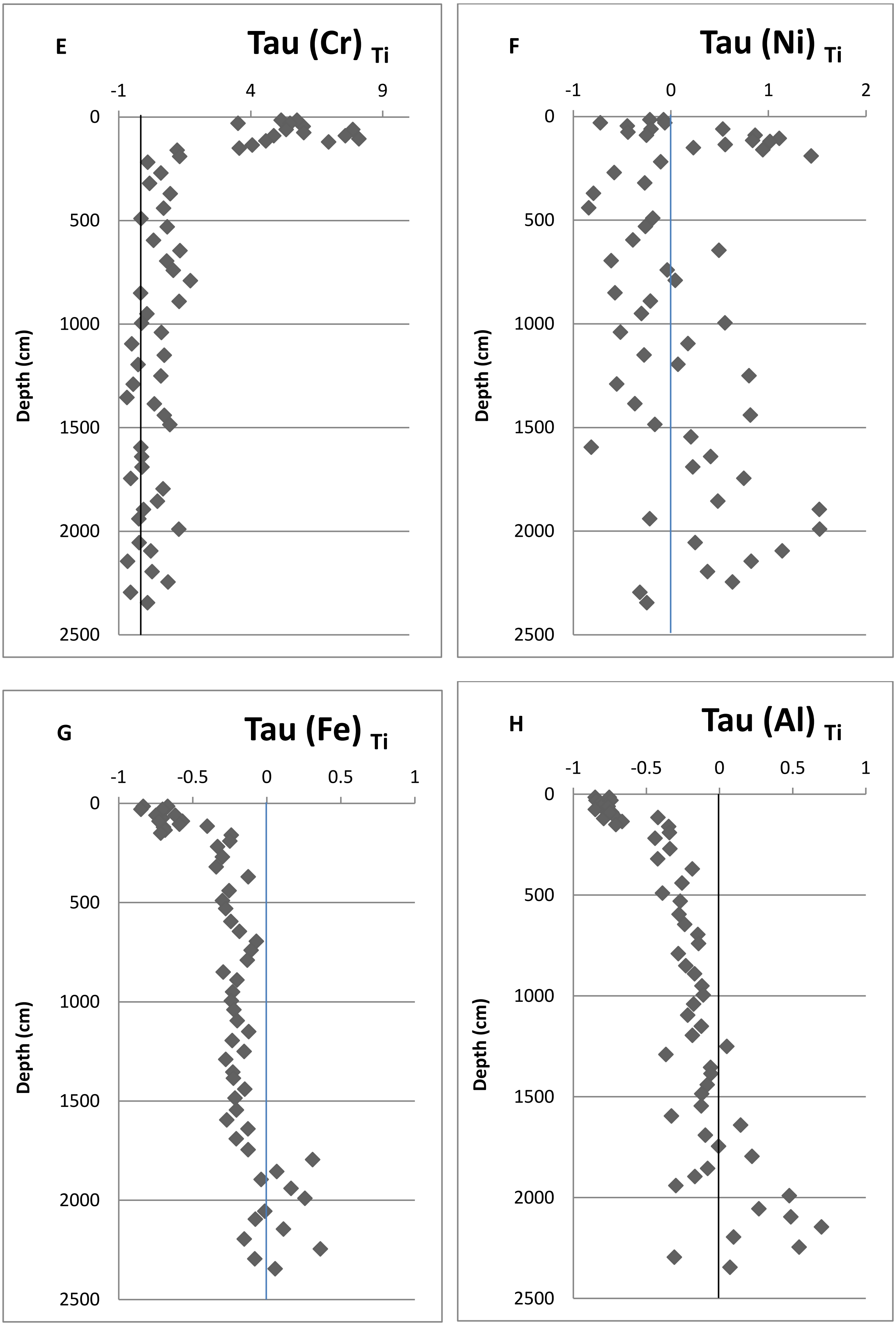
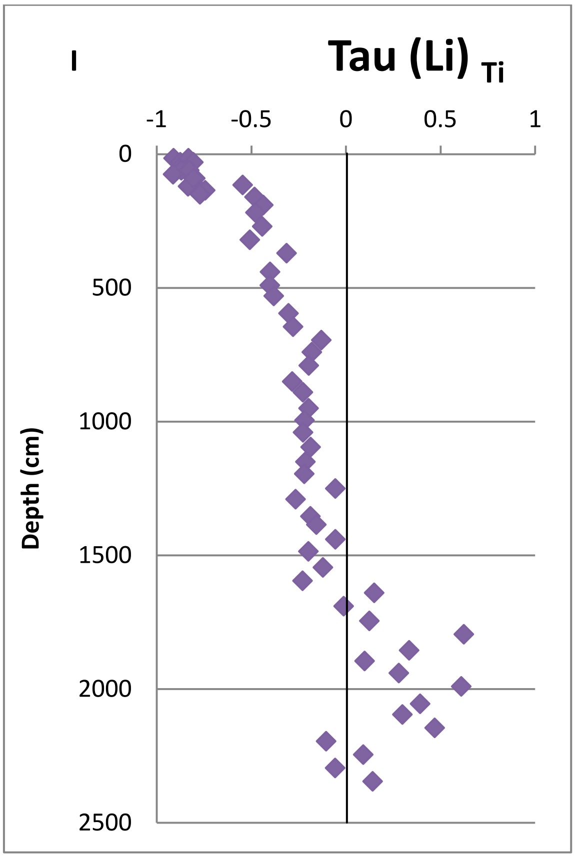
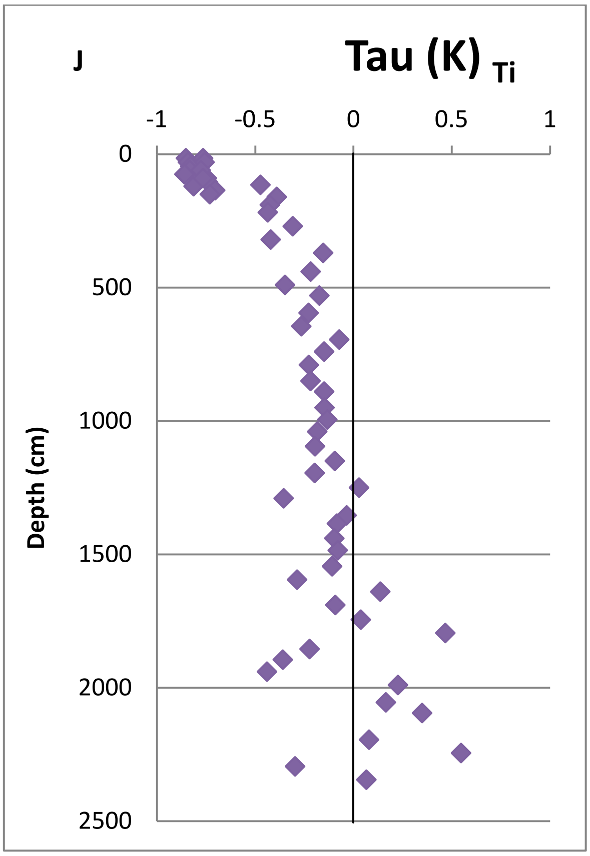

K
Na
Na (ppm)
5000
10000
15000
20000
0
500
1000
1500
2000
2500
Depth (cm)

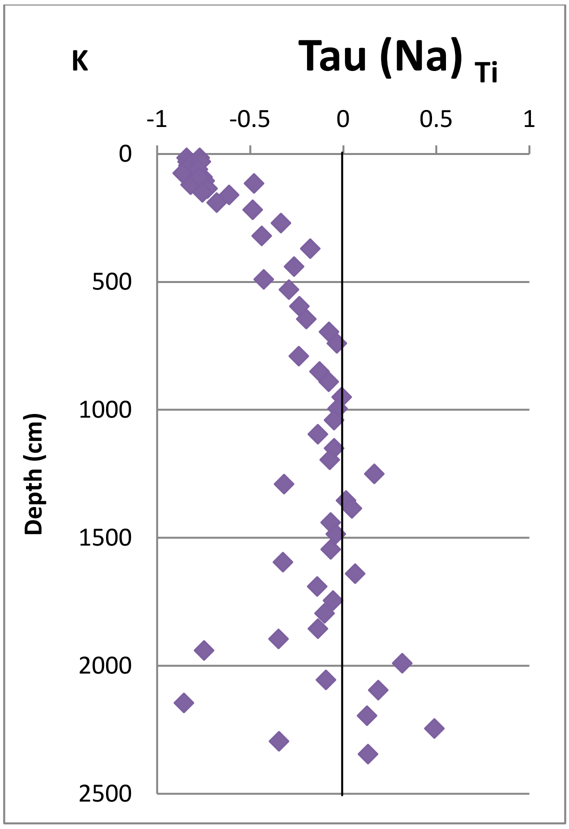
FIG. 8 A-K: THE CALCULATED DEPLETION/ENRICHMENT ELEMENTAL PROFILES (TAU-VALUES) FOR THE STUDIED ELEMENTS IN WEATHERING PROFILE, LYSINA.




E
Tau (Cr) Ti
-1
4
9
0
500
1000
1500
2000
2500
Depth (cm)
F
Tau (Ni) Ti
-1
0
1
2
0
500
1000
1500
2000
2500
Depth (cm)
G
Tau (Fe) Ti
-1
-0.5
0
0.5
1
0
500
1000
1500
2000
2500
Depth (cm)
H
Tau (Al) Ti
-1
-0.5
0
0.5
1
0
500
1000
1500
2000
2500
Depth (cm)


I
Tau (Li) Ti
-1
-0.5
0
0.5
1
0
500
1000
1500
2000
2500
Depth (cm)


J
Tau (K) Ti
-1
-0.5
0
0.5
1
0
500
1000
1500
2000
2500
Depth (cm)


K
Tau (Na) Ti
-1
-0.5
0
0.5
1
0
500
1000
1500
2000
2500
Depth (cm)

5. DISCUSSION

5.1CONCENTRATIONS

5.1.1 Concentration ranges of alkaline earth metals in rock/soil

Our analysis suggest that the least-weathered samples of granite from deepest depth of about 20-25 metres yielded an average calcium (Ca) concentration of about 4000 ppm (from 2900-6500 ppm). In shallow depths from ca. 20 to 4 metres our data show gradual decline in Ca concentration to about 2500 ppm at the depth of 4-5 metres. Finally, the sharpest decline in Ca concentration is recorded in top 4 metres of our weathering profile reaching a minimum of only about 400ppm (Table 4.2).

Contrary to Ca, our analysis revealed that magnesium concentration was relatively low in an average of 700 ppm (from 600-1500ppm) in all the depths recorded. However, significant concentration was depicted in surface depth of about 0.9 to 1.5 metres. Magnesium (Mg) also shows a little abnormality at the depth of 1.6 – 1.9 metres producing unique concentration values 3300ppm and 4000ppm respectively. Unlike Ca, the decline in Mg concentration reaches a minimum of about 300ppm.

In general, the average concentration of strontium (Sr) in rocks shows the lowest values compared to other alkaline earth elements studied. Sr yielded an average of about 14 ppm (from 5-21). The highest concentrations are recorded between 10 – 15 metres of depth, while, the lowest can be found at the depth of 4 – 8 metres of our weathering profile.

Barium (Ba) like Sr indicates relatively low concentration in the rock/soil in the study. Ba shows a systematic trend with highest concentration of about 60 ppm in average (i.e. from 40 – 100) which is recorded in the shallow depth of 1-5 metres. The analyses of our study reveal that the concentration of Ba was in a constant decrease after the depth of 8 metres. However, the lowest concentration was recorded between the depths of 18 – 20 metres. (FIG.7 A-D).

5.1.2 Concentration ranges of metals in rock/soil

Chromium (Cr) is one of the heavy metals studied in our site, and its concentration in rock/soil has an average of about 0.5 ppm (from 0.2- 20 ppm). The sharpest increase in the concentration of Cr was recorded in the top depth (0.2 – 1.2 metres) of our weathering profile. This supports the fact that Cr as a heavy and toxic element was likely released and accumulated through the past decades acid deposition. And because it is not a bio-essential for plants, its abundance at the shallow depth of our regolith is not surprising.

Nickel (Ni) shows the evidence of the most declined elemental concentration in rock/soil among the elements of our study. Although, relatively similar to Cr, the mean concentration of Ni is about 1ppm (ranging from 0.4 – 6.3). It is also of importance to note that the significant concentration of Ni in our weathering profile can be found between 0.15 to 2.0 metres depth. On the other hand, the lowest concentration of -0.08 and 0.18 ppm are recorded at 13.5 and 16 metres respectively.

Iron (Fe) is among the elements with significant concentration in our study site. Our analyses reveal that the least-weathered samples of granite from deepest depth of about 19 – 25 metres produced a mean Fe concentration of about 10,000 ppm (from 6,000 – 12, 000). In the shallow depths from ca. 19 – 2 metres our data show accelerated increment in Fe concentration to about 14,000 ppm at the depth of 3 – 5 metres. However, the highest increase (15,600 ppm) and the sharpest decline (6,089 ppm) were recorded at the depth of 0.6 and 2.2 metres respectively.

Aluminium (Al) shows the highest concentration of all the elements under our study. Besides, the high concentration of Al cuts across all the depths in the weathering profile of our study. Scarcely is there any depth recording concentration below 50,000 ppm. Al indicates an average of 72, 000 ppm (from 48,000 – 87,000). Aluminium has continuously a high concentration of about 73, 000 ppm though there is a slight decline in the concentration after the depth of 17 metres. Our analysis also indicates that between 60,000 – 70,000 ppm of Al were recorded from 18 metres downwards.

Our analytical result shows that lithium (Li) has a rapid increase in its concentration from the shallow to the deepest depth in the weathering profile of our study. Li depicts an average of about 1000 ppm (from 500 – 1900). The lowest concentration of Li which is about 500 ppm is recorded at a depth less than 1 metre. Meanwhile, significant Li concentration which ranges between 1400 to1890 is primarily noticed at the depth of 18 – 21 metres of the weathering profile of our study.

Potassium (K) shows relatively significant concentration. Similar to Al, potassium depicts a trend of constant elemental concentration in the weathered samples of granite from the depth of about 0.5- 25 metres. This yielded a mean of about 25,000 ppm (from 20,000 – 32,000). The lowest concentration of K (1317 ppm) is recorded at the depth of about 21.5 metres of our regolith.

Furthermore, describing sodium (Na) concentration from the shallow depths of ca. 18 – 3 metres, our analysis suggest that the least weathered samples of granite from this depth produced an average Na concentration of about 17,500 ppm (from 12,000 – 18,000). Furthermore, from the deepest depth of 18 – 25 metres, the average concentration of Na is about 14, 000 ppm which is 3,500ppm lower than the concentration value recorded in the shallow depths (FIG.7 A-K).

5.2 TAU - VALUES AND DEPLETION- ENRICHMENT PROFILES

By using the conceptualized analytical method to consider profiles of our concentrations

normalized to the immobile element in parent rock as a function of depth, our analyses revealed and supply tangible evidence to identify the five end-member categories of elemental regolith profiles which were documented by Brantley et al.,(2007). These are depletion profiles, enrichment profiles, enrichment/depletion profiles, immobile profiles, and addition profiles. (See Fig.8 A-K and Table 4.3).

5.2.1 Depletion Profiles

It is important to know that about three-quarter of elements studied show the depletion profile. These include Ca, Mg, Li, Sr, K, Na, Fe, and Al which are here classified in the hierarchical order of their average elemental depletion rates in Tau-values.

In respect to the alkaline earth metals the rate of element depletion follows the systematic trend where calcium (Ca) shows the largest depletion/leaching effect up to -0.97 (Tau-value), which confirms that about 97% of Ca was lost during weathering due to leaching. The second most depleted element is magnesium (Mg) which shows maximum depletion of -0.87 (Tau-value) which indicates that about 87% of Mg is depleted due to weathering. Strontium (Sr) however follows in the depletion trend of other alkaline earth metals which were analysed from the weathering profile of our study. Sr shows up to -0.82 (Tau-value), which proves that about 82% of Sr has been lost during granitic weathering due to leaching.

Iron (Fe) as a transitory metal shows a depletion profile with a leaching effect of up to -0.84 (Tau-value) which emphasized that about 84% of Fe was lost during leaching. Comparatively, aluminium (Al) having indicated a leaching effect of up to -0.84 (Tau), we can conveniently conclude that Al has the same 84% depletion rate as Fe. However, it is of significant note to stress that these depletion are predominantly from the surface/shallow depth ca. 15 – 2.5 metres of the weathering profile in our study.

Furthermore, the alkali metals such as Li, Na, and K under our study generally show depletion profiles though at different degrees or percentages. Lithium (Li) apparently indicates a leaching effect of up to -0.91 (Tau) which confirms that about 91% of Li was depleted. In the same scenario, Na exhibits a leaching effect of maximum -0.86 (Tau), whereas K displays a leaching effect of up to -0.85 (Tau-value). In summary, our analysis revealed that about 86% and 85% elemental losses were recorded for Na and K respectively in our study.

5.2.2 Enrichment – Depletion Profile

Barium (Ba) is an alkaline earth metal which obviously shows enrichment-depletion profile in our study. In the shallow depth ca. 10-3 metres Ba shows up to +4 (Tau-value) which suggests that about 400% of Ba was gained in this weathering profile depth. On the other hand, in the deepest depth of ca. 18.5 -25 metres depletion of about -0.60 (Tau) occurred, signifying that up to 60% of Ba was lost. Apparently, Ba is a typical example of nutrient profile but the exact reason for such behaviour is not yet understood. Ba is an instance of an element which is enriched at the surface but depleted in the deeper depth of the regolith. The combinations of Ba and other elements such as phosphorous might contribute to this enrichment-depletion profile.

5.2.3 Enrichment Profile

Chromium (Cr) is the element that shows the largest enrichment profile up to Tau-values of +8, giving us the interpretation that about 800% was enriched. This enrichment feature of Cr into the ecosystem probably is due to external forces/input from atmospheric depositions such as anthropogenic (coal) and natural (serpentinite) (Quantina et al.2008).

5.2.4 Immobile Profile

Nickel (Ni) exhibits a profile of an immobile element which is similar to those of titanium (Ti). This is a rare case and needs further study in order to fully ascertain the cause of this Ni immobilized behaviour.

6. CONCLUSION

Results showed that Ca, Mg, and Sr all experience significant “depletion” trends toward the top soil, whereas Ba revealed an “enrichment” profile at the shallower depths. Specifically, Ca was highly depleted closer to the organic-rich top soils (tau-values up to -0.97), and Mg also showed a depletion trend but with lower magnitudes (tau-values about -0.84). This observation supports the fact that Ca often out-competes Mg with respect to the intensity of element leaching from the soils and rocks due to weathering and biological processes. Similarly, the normalized weathering profile of Sr showed a “depletion” trend (tau-values about -0.74) that, however, is less pronounced compared to Ca or Mg. In contrast, the normalized weathering profile for Ba yielded a significant “enrichment” trend (with tau-values up to + 4 or 5) whose origin is not currently well understood.

Conclusively, our results from the acidified base-poor forest ecosystem show that the behaviour of alkali earth metals during weathering and soil formation follows a trend where Ca is leached most readily from the system, followed by Mg and Sr. The extremely negative tau-values of Ca, Mg and Sr trends in the upper part of the weathering profile (from -0.74 up to -0.97) are likely a consequence of the long-term and severe acid deposition history at our study site.

The heavy/transitory metals show contrary trends except Fe and Al (tau-values up to -0.85 and -0.84) respectively, which have relatively similarities in their normalized weathering profile as the alkaline earth (Ca, Mg, Sr). The depletion of Fe and Al are of almost same values compared with Mg. However, these were replenished at the deeper depth. On the contrary, the heavy metals (Ni and Cr) with tau-values ranging between +1 up to +8, these are significantly enriched especially Cr in the upper region of the weathering profile.

Calcium has depletion of up to 97% especially in the first 0.15 – 15m depth due to long-term history of soil acidification. Ca is a major nutrient for the growth and development of the forest. Though, the depletion rate continuous to the depth of about 17.5 metres but little enrichment can be observed beyond this depth. This trend supports the point that the trees roots which are mostly found at the upper layer of the soil may have played also some role in this depletion of Ca/Mg as their macro-nutrient. However, leaching due to acidification was likely the primary factor for the surface loss of Ca/Mg. High rate of Aluminium saturation might also account for this decrease of Ca/Mg. Other reasons include leaching and history of acid deposition which lowered the soil pH in this study site.

In the long run, the result of this research project will prove that these two divalent base cations (Ca^{2+} and Mg^{2+}) are constantly in a biogeochemical motion and with high exchange rates at Lysina, Slavkov Forest, Czech Republic. And that the rate at which they are depleted is faster and larger than that of their replacement from mineral weathering or atmospheric deposition. This means that, the availability of Ca and Mg as essential elements for the Norway spruce (*Picea abies*) growth and development is becoming extremely limited. This at present is noticeable among the spruce tree stands around our soil pit and the borehole. Most of them have started to develop stunted growth with yellowish needle and canopies which are symptoms of Ca and especially Mg deficiencies in the soil.

Though in the last few decades, studies have reported that there has been a decline in the atmospheric deposition of acids due to increased campaign on the global reduction of S and N emissions. As the Czech government has put in measures to ameliorate these substance discharges from the industries, especially coal power plants. But this good initiative seems not to resurrect fully the Slavkov Forest and its spruce trees. As discovered in the course of this study and the previous studies, the soil at this site has very low pH level and extremely limited Ca and Mg pools due to intense leaching caused by acid deposition. These will in future pose more danger to the health of the forest in relation to man unless a suitable strategy is put in place to stop this ongoing base cations ‘leaching’ trend.

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8. APPENDICES

Appendix *i: Description table for the drill core samples (Lysina catchment)*

ČGS	**Geological Documentation of Drill Core** **Project:** SoilTrEC No. 667500 **Name of Drill core:** LY-V1 **Page:** 1

Locality	**shaft 's inlet drill-core**	**Recovery**	**Map sheet: 11-411** **locality** 
Kladská-Lysina	**X** 50°2.09783' N	99 %	
Company	**Y** 12°39.61232' E	**Water flow**	
SG IGHG Tachlovice	**Z** 891 m a.s.l.	No	
Model Kits	**Diameter of dril-core**	**Loss of water**	
ADBS, Mercedes Benz Atego	175 mm preborehole 89 mm conductor casing (0-3.4 m) 76 mm borehole (3.4-30.3 m)	Yes	
Date 3.–4. 9. 2012	**Type of drill-core** vertical core	**Depth of drill-core** 30.30 m	
Driller	**Documentation**	**Date of photo documentation**	
Marek Topinka	Tomáš Jarchovský Veronika Štědrá	3.–4. 9. 2012	

Photo of drill core **(cca 1 : 10)**	**Depth (m)**	**Description**	**Petrology and Minerology**	Samples

	0,0	black forest soil	**Q** Quaternary, soil	
	0,30 ∅ 170 mm	sandy slope soil with granite fragments	**Q** Quaternary, slope sediments	
	1,50	sandy residuum, pale grey, strongly weathered, decomposed granite	**G** granite	H 2,77

	3,40 ∅ 76 mm	solid fine-grained granite, in places porphyritic Fs porphyrocrysts up to 1 cm, quartz up to 5 mm - in places euhedral Tectonized section: 3,40–4,0	**Gp** porphyritic granite	►4,60 GCH 4,65
		Tectonized section 5,30–6,10 m	*Gp* porphyritic granite	
	6,50	firm but crashed core with unsharp transition to medium grained granite, Feldspars porphyrocrysts only rarely, up to 1–2 cm	*G* medium-grained, weakly porphyritic granite	►7,05 GCH 7,10
	8,0	medium grained granite, pinkish, weakly altered	G medium-grained granite	*N 9,83*
		9,0–9,40 m Core is crushed	G medium-grained granite	

	11,0	reddish tint of granite due to alteration of K-feldspars, with unsharp transition to light granite at m 12,70	G light granite	►*12,60 GCH 12,65*
	14,0	tectonized section with weak alteration	G light granite	
	15,0	solid granite with very weak alteration, tectonized section at 15,60 -16,10 m	G light granite	*N 15,18* *N 18,10* ►*18,20 GCH 18,25*
	18,30	Solid medium-grained G. Qtz in the form of drop-like grains At 19,40 m subvertical crack 5 mm wide filled with grey quartz	medium-grained granite	
	19,40	Medium-grained granite coloured by haematite disseminated through,	medium-grained granite	
	20,30	mylonitized zone with haematitic alteration 20,30–21,20 m	mylonite	

	 21,20	continues solid fine-grained G with haematite dusting	G fine-grained granite rich in K	
	21,45	Solid pinkish fine-grained granite	G fine-grained granite rich in K	*►22,30* *GCH* *22,35* *N 22,41* *H 23,68*

	 25,20	unsharp transition to fine-grained porphyritic granite with feldspars up to 1–2 cm	Gp fine-grained porphyritic granite rich in K	*H 25,63* ►*25,95 GCH 26,00*
	27,20	Tectonized zone: 27,20–27,40 m	G medium-grained granite, tectonized	►*27,20 GCH 27,25*

	 27,40	Solid fine- to medium-grained granite with rare K-feldspar porphyrocrysts 1–2 cm long	G medium-grained granite	
	28,40	Creamy coloured medium grained granite (the Lysina type), fresh, without porphyrocrysts, in places almost coarse-grained (30,00 m)	G medium-grained granite	*H 28,75* *N 29,55* *►30,10* *GCH 30,15*
	30,30	The end of the drill hole		

Appendix *ii*: LYSINA SOIL PIT SAMPLE (I-X)- THE NON-HOMOGENIZED SAMPLE

Sample Identification	Depth (cm)
I – LY	15
II – LY	30
III – LY	45
IV – LY	60
V – LY	70
VI – LY	90
VII – LY	105
VIII – LY	120
IX – LY	135
X – LY	150

Appendix *iii*: Mineralogical description of thin sections from a drill-core, Lysina (Tomáš Jarchovský and Veronika Štědrá, Czech Geological Survey).

DEPTH 4.60m (460cm)	
ELEMENT	**DESCRIPTION**
QUARTZ	Has anhedral grains up to 1 mm and is mostly in the intergranular spaces, with globular margins. There are also trails of microscopic fluid inclusions, rarely with platy dark brown mica and topas crystals.
FELDSPAR:	
K-Feldspar	This is the major mineral in this depth. It forms platy crystals more than 10 mm long, perthitic, hazy with numerous inclusions of minor flakes
Plagioclase Feldspar	These are also seen in this depth with good crystal shape.
MICA:	
Biotite Mica	Brownish/dark reaction zones around small crystals of accessory zircon. This dark mica mineral are common at this depth.
Muscovite Mica	Whitish/clear forms flakes up to 2 mm, with irregulat boundaries, pleochroic from weakly creamy to brownish, in cross-sections almost colourless. Along margins, colourless muscovite forms the younger margins
TOPAZ	common as grains and crystals enclosed in secondary fine-grained coronas of light mica, as irregular grains up to 1 mm. Mica and sericite replace it along cleavage planes. Occassionally present complete pseudomorphs are composed of sericite and flaky clay mineral.
DEPTH 7.05m (705cm)	
QUARTZ	isometrix grains, with rare parallel trails of fluid inclusions, and includes minor dark brown Li-biotite flakes. In the matrix, it reaches 0.1 mm in size.
FELDSPAR:	
K-Feldspar	40 vol. % , hazy crystals with perthitic structures
Plagioclase Feldspar	tabular crystals 5–7 mm in length.
MICA:	
Biotite Mica	weakly brownish irregular flakes in the matrix.
Muscovite Mica	colourless, irregular flakes.
TOPAZ	Very rare in this depth. Seen as only one small grain.
DEPTH 12.60m(1260cm)	
QUARTZ	Quartz reach up to 5 mm. It is anhedral, intergranular between platy Fs crystals. Contains numerous systems of inclusion trails of variable directions, and tiny biotite tabular crystals.
FELDSPAR:	
K-Feldspar	Often hazy, along cleavage planes transformed to sericite.

Plagioclase Feldspar	Sericite common also along grain boundaries and cracks. Some seriricte aggregates involve also fine-grained aggregates of fluorite. It reaches up to 5 mm.
MICA:	Dark brown pleochroic spots around tiny radioactive accessory minerals. It also has weakly colourless flakes with irregular rims which might be of muscovite origin.
Biotite Mica	
Muscovite Mica	
TOPAZ	Frequent but partially decomposed grains, usually bright colourless, surrounded by secondary micas and clay minerals.
DEPTH 18.80m (1880cm)	
QUARTZ	Very rich in quartz with irregular shape.
FELDSPAR:	Kfs and Na-Pl together predominate, are affected by seritisation along cracks and cleavage or even pseudomorphing magmatic crystals.
K-Feldspar	
Plagioclase Feldspar	
MICA:	5–8 volume percentage is disseminated in the rocks as weakly brownish flakes of irregular shapes, without accessories or inclusions.
Biotite Mica	
Muscovite Mica	
TOPAZ	This occurs as relict grains in pseudomorphs formed of fine spots of fibrous to platy sericite.
DEPTH 22.30m (2230cm)	
QUARTZ	Quartz is represented less than in other samples, however, the inclusion trails are present here as well.
FELDSPAR:	This is dominant at this depth. It creates subhedral platy crystals up to 5 mm, partially altered and hazy, containing minor flakes of sericite and white mica, the latter with lobate shapes.
K-Feldspar	
Plagioclase Feldspar	
MICA:	Abundant light mica forms aggregates and single grains with irregular rims. Mica is whitish or colourless, is probably partially leached, and does not include grains or any colour contact effect. There is haematite exsolved along cleavage planes. Mica in places intergrows with K-feldspar grains and forms skeleton textures. Sericite-haematite aggregates fill intergranular spaces between feldspar and mica crystals. Haematite is disseminated as a weak fine-grained dusting all over the rock.
Biotite Mica	
Muscovite Mica	
TOPAZ	Shows a form of accessory mineral, often occurs in relics encompassed by secondary minerals or is included in albite as minor clear grains.
DEPTH 25.95m (2595cm)	
QUARTZ	Quartz represents 40–50 vol. % and is rather abundant. Quartz grains here are usually rounded, often in aggregates up to 5-8 mm, with fluid inclusion trails

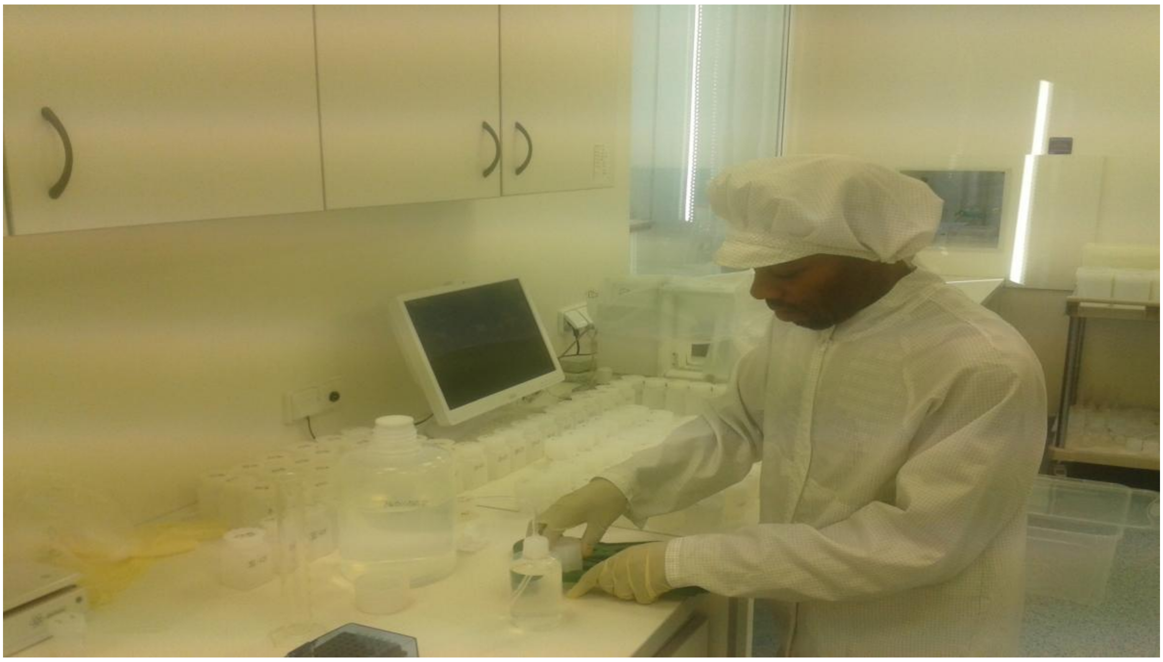
FELDSPAR: K-Feldspar Plagioclase Feldspar	Feldspars are only weakly altered, albite displays well developed twinning lamellae and is les altered than K-Fs which is more abundant and forms platy crystals of 6 mm in length.
MICA: Biotite Mica Muscovite Mica	Light-mica is weakly brownish, forming flakes of irregular shapes to skeleton-type, 1–2 mm in size. Occurs often in intergranular spaces. Contains frequent pleochroic circles around accessory mineral inclusions, needle-shaped of opaque wolframite.
TOPAZ	Topas is usually in aggregates of subhedral grains, with irregular cracks. Topas rarely encloses fine tables of albite.
DEPTH 27.20m (2720cm)	
QUARTZ	Quartz – (50 vol. %) in aggregates of anhedral grains with fluid inclusion trails. It often encloses minor flakes of dark brown Li-biotite in central zones of grains.
FELDSPAR: K-Feldspar Plagioclase Feldspar	Abundant K-Fs (ca 40 vol. %) is weakly hazy, ecloses fine grains of sericite and muscovite with disseaminated haematite dusting.
MICA: Biotite Mica Muscovite Mica	Li-mica is markedly brownish, is more common than in other samples - up to 10 vol. %. Dark brown tint is speci´ficly bound to pleochroic zones around enclosed accessory minerals and along cleavage cracks. In places, younger muscovite forms a colourless outer growth zone of crystals. This mica is far rich in titanum.
TOPAZ	Topaz occurs in individual relict grains surrounded by aggregate of replacing minerals like sericite and clay minerals.
DEPTH 30.10m (3010 cm)	
QUARTZ	Quartz – forms isolated anhedral grains or their clusters with undulatory extinction, up to 10 vol. %. Usually in spaces between tabular feldspar crystals, it contains often fluid inclusion trails.
FELDSPAR: K-Feldspar Plagioclase Feldspar	Abundant K-Fs (ca 40 vol. %) forms grains up to 3-7 mm, is weakly hazy, ecloses fine grains of sericite and muscovite with disseminated haematite dusting and perthitic exsolutions.
MICA: Biotite Mica Muscovite Mica	Li-mica in less abundant than in previous samples, forms up to 5 vol %, irregular tiny flat crystals, is weakly brownish, Albite – almost clear, without alterations, usually as subhedral flakes with tiny grains of white mica.
TOPAZ	Topaz usually as individual relict grains up to 1 mm surrounded by aggregate of replacing sericite and clay minerals or completely replaced by their mixture.

Appendix iv: Drill core photographs on devices for mechanical work I (photo: AUTHOR)

Appendix v: Drill core photographs on devices for mechanical work II (photo: AUTHOR)

Appendix *vi:* Photograph showing the soil pit (Lysina) *(photo: AUTHOR)*

Appendix *vii*: photographs showing samples from the drill core (Lysina) *(photo: AUTHOR)*



Appendix viii: Czech Geological Survey Laboratory-Dissolution of Silicates (*photo: AUTHOR*)

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