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Chemical weathering of mafic rocks in boreal subarctic environment (northwest Russia) under influence of glacial moraine deposits

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Abstract

Chemical weathering of mafic rocks represents substantial sink of atmospheric CO₂ yet the mechanisms of this process in high-latitude regions are poorly understood. This work addresses geochemical migration and partitioning of major and trace elements between rock, soil and surface waters during chemical weathering of mafic rocks and soil formation under the influence of a glacial moraine in the northwestern Russian subarctic. We used multidisciplinary approach which included major and trace element chemical analysis, Sr isotopic measurements, and mineralogical structural and microscopic investigations. Quaternary (Pleistocene) deposits were observed even in the deepest horizons of soil profiles and confirm a strong moraine influence as most soils showed podzolic features. Chemical and Sr isotopic analyses revealed a strong impact of the moraine on soil chemistry and mineralogy. Mineralogical studies showed the presence of non-aeolian quartz and zircon in soils which were not linked to the nature of the parental rocks (i. e. mafic and felsic). At the same time, we observed the presence of etch pit corrosion on the surface of zircons and feldspars, and a newly-formed matter adjacent to the surface of primary phases. The chemical index of alteration (CIA) showed weak or no weathering of rocks within the soil profile and the weathering intensity scale confirmed the “felsic” chemical composition of soils developed over mafic and ultramafic rocks. Analysis of Sr radiogenic isotopes demonstrated preferential removal of easily weatherable and less radiogenic minerals over the full depth of soil profile and a more radiogenic signature of the granitic moraine compared to mafic and felsic bedrocks. The composition of most surface waters reflected the weathering of silicate rocks but did not allow for distinguishing purely mafic source. The chemical weathering rates of ultramafic rocks were calculated to be higher than those for the granitic till, but the moraine depositions which dominate this region hide evidence of the real weathering process. This could be due to retention of Mg and Ca in soil due to precipitation of secondary phases such

as Mg-vermiculite or divalent cation adsorption on mineral, organic or organo-mineral phases. As a result, weathering rates estimated for the olivinite rock appear to be lower than the weathering rates of mafic rocks reported in other boreal and subarctic regions. Overall, the felsic moraine deposits are capable to sizably decrease the weathering intensity of mafic rocks which should be taken into account for chemical weathering modelling of high-latitude regions subjected to glaciation in the past.

1. Introduction

Numerous works have emphasized the significant role of silicate weathering in atmospheric CO₂ consumption and climate regulation; it is considered to be the principal process for removing carbon dioxide from the atmosphere on a long-term scale (Berner et al., 1992, 1995; Boeglin and Probst, 1998; Berner and Caldeira, 1999; Gaillardet et al., 1999; Kump et al., 2000; Dupré et al., 2003). Weathering of continental basalts, accounting for about 30 % of total CO₂ consumption by silicate weathering (Dessert et al., 2003), has been extensively addressed (Gislason et al., 1996; Louvat and Allègre, 1997, 1998; Dessert et al., 2001; Grard et al., 2005; Pokrovsky et al., 2005, Schopka et al., 2011; Gaillardet et al., 2011, Schoppa and Derry, 2012; Eiriksdottir et al., 2013, 2015; Balagizi et al., 2015; Dessert et al., 2015; Ibarra et al., 2016). Recently, it has been shown that the weathering of silicate and carbonate rocks in the Baltic Sea catchment accounts for 3 to 30% of the net ecosystem C exchange, implying that weathering represents a significant sink of atmospheric CO₂ (Sun et al., 2017). In contrast, very few investigations dealt with the impact of chemical weathering on soil formation and CO₂ consumption in the environment underlain by intrusive mafic rocks such as gabbros and olivinite (Schroeder et al., 2000). There are relatively few studies on comparative weathering intensity of acidic versus basic silicate rocks at the catchment scale (Horton et al., 1999; Ibarra et al., 2016; Wymore et al., 2017). Notably, in the Karelia and

Kola provinces (northwestern Russia, see **Fig. 1**), cationic weathering fluxes estimated from river water chemical compositions and daily discharges are among the lowest in the world: TDS_c = 0.33 and 2.3 t/km²/yr for granite and basaltic watersheds respectively (Zakharova et al., 2007). Surprisingly for mafic rock dominated watersheds, the Baltic Shield values are only half the value measured for central Siberian basalt (~5 t/km²/yr, Pokrovsky et al., 2005) despite similar runoff but sizeable mean annual air temperature (MAAT) differences (+1 ± 2°C in Karelia versus -9 ± 2°C in Central Siberia). Such a disagreement does not allow reliable extrapolation of the widely used “temperature-basic rocks weathering intensity” relationship (Dessert et al., 2003) for specific subarctic environments in the present and past. Further, the temperature sensitivity of chemical weathering is recognized to be strongly limited by river discharge and water residence time in soils (i.e., Maher, 2011; Maher and Chamberlain, 2014; Ibarra et al., 2016; Raymond, 2017 and references therein). Therefore, studying the weathering mechanisms at the soil and small catchment scales is necessary to explain the differences in mafic rock weathering in Europe and Siberia and to reveal the factors responsible for slower weathering rates under specific environmental conditions present in NW Russia. Recently, strong interest to chemical weathering linked to widespread deglaciation processes (i.e., Foster and Vance, 2006; Stroeve et al., 2016) has been focused around Greenland Ice Sheets (Andrews et al., 2014; Hindshaw et al., 2014; Deuerling et al., 2018), Arctic Islands (Hindshaw et al., 2016), and Iceland (Opfergelt et al., 2014; Hawley et al., 2017).

In contrast to the western European boreal environments located in the vicinity of the Baltic Sea that are housed in a relatively mild climate, the understanding of the geochemistry of ecosystems situated along the Arctic sea coast, including the White Sea, still remains quite poor. The Karelia and Kola provinces (northwestern Russia) belong to this zone and offer possibility to study the weathering of the coexisting mafic (e. g. olivinite, gabbro-norite) and

felsic (e. g. gneiss, granite) rocks within a relatively small and therefore easily accessible spatial scale. The region is characterised by the presence of abundant glacial moraine and till deposits. In Finland, different genetic moraine types (e. g. ground moraine, Rogen moraine, Pulju moraine, Sevetti moraine, Kianta moraine, De Geer moraine, etc.) were determined according to the classification given by Hättestrand (1997) and their geochemistry, mineralogy and morphology were extensively studied (e.g., Peuraniemi, 1982; Zilliacus, 1989; Peuraniemi et al., 1997; Sarala, 2005, Lunkka et al., 2013). The chemical and mineralogical composition of the moraine that covers the study area (northern and southern Karelia) suggest it was formed from Quaternary deposits of Pleistocene age (Evdokimova, 1957; State Geological Map of Russian Federation, 2001). Soil ages in this zone are supposed to be around 10 Ky. According to Thiede et al. (2001), Karelia and the Arkhangelsk regions were covered in ice sheets only during the late Weichselian glaciation phase (i. e. 17-15 Ky). Supposedly, during this period the soil erosion process was so important that almost all the soil cover disappeared in contrast to more southern regions (Salminen et al., 2008) where soil profile ages vary from 60 to 150 Ky.

Cool and humid boreal regions of Europe are dominated by podzolic soils extensively described in Russia (Dokuchaev, 1880; Ponomareva, 1964) and western Europe (e.g., Muir, 1961; Anderson et al., 1982; Buurman, 1984; Righi and Chauvel, 1987; Lundström, 1993; Courchesne and Hendershot, 1997, van Breemen and Buurman, 1998; Lundström et al., 2000, 2000a; Buurman and Jongmans, 2005). Podzols are typically found on coarsely textured base-poor parent materials such as sands and sandy tills, and are often located in Precambrian Shield granitic/gneissic environments (Lundström et al., 2000). However, podzol type soils were also described in mafic and ultramafic environment under boreal climate (e. g. Lesovaya et al., 2008; Salminen et al., 2008). The occurrence of podzol type soils over mafic rocks is also suggested in the World Reference Base for soil Resources (IUSS Working Group WRB,

FAO, 2006); however, considering the most used taxonomic systems criteria, only few of those podzol type soils which developed over mafic rock could be classified as a true podzol. Indeed, even if soils show a podzol like morphology (i. e. occurrence of an eluvial “albic” horizon overlying a reddish-brown illuvial “spodic” horizon), the pH of these soils are usually too high compared to classic podzols (D’Amico et al., 2008). According to D’Amico et al., in such a case, the podzolisation process is favoured by the occurrence of quartz-rich allochthonous material such as aeolian deposit or till. The question of the role of moraine deposits in boreal podzol pedogenesis under a granitic environment was also raised by a number of recent works devoted to the study of mineralogical and major and trace element composition (as well as calculation of weathering losses) of podzols and spodosols developed on granite-gneiss glacial moraine deposits in northern Europe (Öhlander et al., 1991, 1996, 2003; Giesler et al., 2000; Melkerud et al., 2000; Olsson and Melkerud, 1989, 2000; Land and Öhlander, 2000; Land et al., 1999, 1999a, 2002; Tyler, 2004; Starr and Lindroos, 2006). Lundström et al. (2000a) reported results of a multidisciplinary study (combining geochemical, mineralogical, micromorphological, microbiological, hydrochemical and hydrological investigations) aimed at testing various mechanisms (adsorption/precipitation versus biodegradation) controlling the formation of podzols in glacial till context. Clay mineralogy and chemical weathering of soils in a recently deglaciated arctic-alpine environment in Sweden were studied by Allen et al. (2001). The authors suggest that the occurrence of mixed layer minerals could be a tracer of parental rock weathering in soils affected by moraine deposits. Contrastingly, Akselsson et al. (2006) found that there is no relation between elemental content and mineralogy of till and bedrock mineralogy for podzolic soil in southern Sweden and concluded that the information on the bedrock is not sufficient for prediction of till mineralogy.

In northwestern Russia chemical and mineralogical composition of soils developed on nepheline syenite, amphibolite and metamorphized diabase that were affected by moraine deposition were recently studied by Lesovaya et al. (2008). These authors argued that soil profiles became thicker and showed notable clay mineral transformation when allochthonous moraine material is intermixed. In a more recent study (Lesovaya et al., 2012), the same team studied chemical weathering processes of mafic rocks in the polar Ural and emphasised weathering of smectite and secondary iron hydroxide accumulation in relation with acidification processes (biota effect) which are unusual in ultramafic environment. Thus, despite these aforementioned studies on soil formation and chemical weathering processes in boreal environment, there is still a lack of studies devoted to soil forming processes on mafic rocks and related river hydrochemistry under glacial moraines.

Towards improving our understanding of mafic rocks weathering in boreal climate, we use a multidisciplinary approach which is comprised of studying the geochemical migration and partitioning of major and trace elements between different reservoirs (rocks and soils), major and trace elements analysis, Sr and Nd isotopic measurement, and mineralogical investigation. We aimed at characterizing rock weathering rates and adjacent rivers hydrochemistry in order to understand the soil forming processes on basaltic rocks in the boreal zone influenced by glacial moraine.

For this, we studied mafic and felsic rocks, as well as soil and water samples collected within the Kivakka (northern Karelia) and Vetreny Belt (southeastern Karelia) magmatic formations that are bounded by Archean age crystalline granitic rocks. The main questions we attempt to answer in this study are: *i*) “to what degree the presence of a granitic-gneissic moraine can modify the weathering features of basic rocks and degree of element leaching from these rocks?”, *ii*) “what are the differences between different mafic rock (gabbro, norites, peridotites, olivinites, and basalts) degree of alteration in soils under the same

environmental conditions (climate, vegetation)?” and *iii*) “how contemporary weathering processes are reflected in surface and soil water chemical compositions?”

2. Geological and geographical setting

The Vetreny Belt paleorift and the Kivakka layered intrusion are situated in the Karelian region of northwestern Russia and exhibit similar geological, climatic, and hydrological conditions. The main difference between these two sites is the nature of their mafic rocks: gabbro-norite (peridotite) create the Kivakka intrusion and basalts with some olivinites create the Vetreny Belt.

2.1. Lithology, soils and vegetation

The Karelian region is situated in the north-western part of Russia, bordering Finland to the west, Lakes Ladoga and Onega to the south, and the White Sea – an extensive gulf of the Arctic Ocean – to the east. Largely a hilly plain, the region has mountains in the west with elevations up to 600 m. The lowest elevations are near the White Sea and the many lakes that have filled depressions scoured across the surface during the last glaciation period. The relief of Karelian zone was formed under the influence of glaciation which occurred at least 3 times during Pleistocene (Reimann and Melezhik, 2001) with and the last glacier disappearing about 20-10 thousand years ago.

The study area is also a part of the Eastern Fennoscandian Shield. A simplified map of the two chosen sites along with sampling points and some geological information are given in **Fig. 1**. Quaternary deposits consist primarily of coarse-grained and sandy till or glaciofluvial deposits showing well-developed podzol profiles. Detailed information of major and trace element composition of volcanic rocks and rock-forming minerals utilized in this work can be found elsewhere (Amelin and Semenov, 1996; Koptev-Dvornikov et al., 2001; Bychkova,

2003; Bychkova and Koptev-Dvornikov, 2004; Bychkova et al., 2007 for the Kivakka layered intrusion; Kulikova and Kulikov, 1981; Ryabchikov, 1988; Puchtel et al., 1996, 1997; Kulikov, 1999; Kulikov et al., 2005 for the Vetreny Belt; Lobach-Zhuchenko et al., 1986, 1993; and Bibikova et al., 2005 for the Archaean granitic and tonalitic gneisses surrounding the chosen intrusions).

The main part of the studied zone belongs to a boreal taiga forest ecosystem with pine, fir, birch, ericaceous species, and mosses that cover more than 80 % of the territory. Approximately 20 % of the territory is covered by wetlands that were developed on thick peat and gley-podzol soils. On well-drained territories alluvial-ferruginous-humic and alluvial-humic podzols prevail. They are developed under pine- and spruce-pine forests with moss-fruticulose cover. The soil depths in the region vary from 30-40 cm in the northern part and 60-85 cm in the southern part of Karelia. On the hill tops (100-200 m) soil depths do not exceed 10-20 cm. Ferruginous podzols are remarkable for high acidity, especially in superficial horizons (Lundström et al., 2000a and references therein). Soils are partly developed on a glacial granite moraine which consists mainly of sand and loamy sand with gravel and boulder inclusions. The glacio-lacustrine and lacustrine as well as fluvio-glacial deposits commonly form in lenses and are wide spread (Zakharova et al., 2007).

2.1.1. Vetreny Belt paleorift

The Vetreny Belt (63°46'N – 35°48'E) (**Fig. 1**, left) is situated in the south-eastern part of the Baltic Shield on the territory of the south-eastern Karelia and Arkhangelsk regions. It occupies a territory of approximately 5200 km² and can be traced from Lake Vyg southeastward over a distance of more than 250 km. Its width increases from 15 to 85 km to southeastward where it plunges beneath Paleozoic cover of the Russian platform and extends further southeast (Kulikov et al., 2003). A detailed description of the Vetreny Belt suite is

given by Puchtel et al. (1997) who also suggested that massifs like Kivakka layered intrusion have an origin related to the Vetreny Belt volcanic and plutonic rocks. The Vetreny suite consists entirely of a thick unit of basaltic komatiites belonging to the Sumian and younger groups in the area (Kulikov and Kulikova, 1982). The isotopic dating of the Vetreny belt yielded the following ages: 2449 ± 35 Ma and 2410 ± 34 Ma (Sm-Nd), 2424 ± 178 Ma (Pb-Pb), 2437 ± 4 Ma (U-Pb) (Puchtel et al., 1997).

2.1.2. Kivakka layered intrusion

The Kivakka pluton ($66^{\circ}12'N - 30^{\circ}33'E$) (**Fig. 1**, right) is located in northern Karelia and belongs to a complex of layered peridotite-gabbro-norite intrusions in the Olanga group that hosts migmatized biotite and amphibole gneisses, granite-gneisses, and granodiorite-gneisses of Late Archean age (Lavrov, 1979; Amelin et al., 1995). In addition to the Kivakka pluton, the group includes the Lukkulaivaara and Tsipringa massifs (Shmygalev, 1968; Lavrov, 1979; Klyunin et al., 1994; Semenov et al., 1995; Amelin and Semenov, 1996). All of these are spatially restricted to an east-west trending regional fault zone and comprise the eastern branch of an extensive belt of layered massifs whose western branches continue across Finland (Alapieti, 1982). Detailed geological and petrological descriptions of the Kivakka layered intrusion can be found in the work of Koptev-Dvornikov (2001). The isotopic dating of the massif yielded the following ages: 2420 ± 23 Ma (Sm-Nd), 2445 ± 3.4 Ma (Zr) and 2444 ± 1 Ma and 2445 ± 2 Ma (Amelin and Semenov, 1990, 1996; Barkov et al., 1991; Balashov et al., 1993).

2.2. Climate and hydrology

The climate of most of the territory is mildly cold, transitioning between oceanic and continental, with a dominant influence of the Arctic and Northern Atlantics. Snow period lasts

from October through April-May with snow cover thickness ranging from 70 up to 110 cm. Mean annual temperature is close to 0°C but extremes can reach as high as +35° and as low as -35°C in summer and winter periods, respectively. Mean precipitation amount is between 400 and 600 mm/yr.

The region has a well-developed river network that flows via a system of glacial lakes. Chemical composition of river water in Karelia is determined by chemical weathering of silicate parent rocks of the Baltic crystalline shield, quaternary deposits, and the presence of numerous peatlands. Typical values of total dissolved solids (TDS) for this region are 15-30 mg/l (Maksimova, 1967; Zakharova et al., 2007) and the concentration of suspended matter in the river is very low. The study region can be considered as pristine, although some influence from Kola peninsula smelters can be pronounced via long-range atmospheric pollution (i. e. de Caritat et al., 2001).

3. Materials and methods

3.1. Sampling of rocks, soils, surface waters and soil pore waters

A list of soil, water, and soil water samples as well as their bedrock composition is presented in **Table 1**. For both soils and waters, series named “V” and “K” correspond to samples collected within the Vetreny Belt paleorift or Kivakka layered intrusion zones, respectively. Three altered rocks – an Archean gneiss, basalt, and peridotite – were sampled within the Vetreny Belt intrusion zone while two other basic rocks – a gabbro-norite and olivinite – were sampled from Kivakka layered intrusion in order to investigate formation of secondary phase minerals in thin sections. Ten soil profiles, five from each study site and five from each type of mafic and felsic parent rocks were sampled for pedological, mineralogical and chemical analysis (see **Table 1** for description and **Table SI-1** of **Supplementary Information 1** for chemical composition of soils).

Small and large rivers, as well as several wetlands and soil pore waters draining through mafic and felsic rocks were sampled during extensive field campaigns in July 2004 and July 2006 for dissolved major and trace elements contents. Each location was sampled only once. Three types of water were chosen for this study: river water, bog water, and interstitial soil solutions draining from both felsic and mafic rocks (see **Table 1** for description and **Table 2** for chemical composition of waters).

3.2. Analytical techniques

3.2.1. Mineralogical and chemical analysis of rocks and soils

Mineralogical studies on altered rock material were made on polished consolidated thin sections using optical microscopy, scanning electron microscopy (SEM GEOL 6360LV coupled to EDS PGT SDD SAHARA) including X-ray microanalysis, and electron microprobe analysis (CAMECA SX50) in the GET laboratory (Toulouse). Modal composition of the different altered rock samples was calculated by using structural formulae of minerals and chemical composition of parental rocks and was coupled with SEM information. Analysis of clays in soil sample K-14 (C horizon) was performed by transmission electron microscopy (TEM) in the CRMCN laboratory, Paul Cézanne University, Aix-Marseille III, France.

The individual composition of soil minerals was determined by SEM with EDS on soil grain thin sections. Afterwards, a structural X-ray diffraction analysis (XRD) was performed on soil clay fractions in the GET laboratory (Toulouse). Clay fraction (i. e. < 2 μm grain size) was separated by decantation in water column. Furthermore, structural XRD analysis performed on INEL G3000 Cu $K\alpha_{1,2}$, oriented samples were prepared by dropping of < 2 μm suspension on a glass plate and drying it at room temperature. Standard treatment (H_2O , ethylene glycol, and heating at 500°C) was employed to assess the interlayer distances of clay minerals.

After crushing, pulverization, and homogenization, soil samples were digested in H₂O₂ at 25°C for 24 h and then in HF-HNO₃-HCl on a hot plate at 60-120°C in Teflon beakers in a clean room (classes between 5 and 7 according to the ISO 14644-1 standard). The validity of total chemical analysis for soils was verified by applying the same procedure for international geostandards BE-N (i. e. basalt), GA and AC-E (i. e. granites) for rocks, and LKSD-1 (i. e. lake sediment) for soils. Trace elements in rocks and soils were analysed by ICP-MS with an uncertainty < 10 % for the elements presented in this study. Indium and rhenium were used as internal standards. Major elements in soils were analysed by ICP-AES method in SARM laboratory (Nancy, France) and ALS Chemex laboratory (Vancouver, Canada). The analytical error of these measurements was in the range 5-10 %.

Total organic carbon (TOC) was analysed in dried soils by a Horiba carbon/sulphur analyzer EMIA-320V with an uncertainty better than 10 %. Soil pH was measured in deionised water suspension according to international ISO norms for measuring soil pH (AFNOR, 1996, ISO 10 390). The accuracy of measurements was ± 0.05 pH units.

3.2.2. Chemical analysis of river, mire and soil pore waters

Physico-chemical parameters of unfiltered water samples (pH, temperature ($\pm 0.2^\circ\text{C}$), and electrical conductivity) were measured in the field. The pH was measured using a combined Schott-Geräte electrode calibrated against NIST buffer solutions (pH = 4.00 and 6.86 at 25°C), with an accuracy of ± 0.02 pH units. Samples were collected from near the middle of the flow channel, using 1-l high-density polyethylene (HDPE) containers held out from the beach on a non-metallic stick. Vinyl gloves were always used during handling of the samples. The water samples were immediately filtered through sterile, single-use Minisart[®] filter units (Sartorius, acetate cellulose filter) with pore sizes of 0.45 μm . The first 200 ml of the filtrate were systematically discarded. Filtered solutions for cations, trace element and Sr

isotope analyses were acidified ($\text{pH} = 2$) with ultrapure double-distilled HNO_3 and stored in HDPE bottles previously washed with ultrapure 0.1 M HCl and rinsed with MilliQ deionized water. Filtered water samples for anions were not acidified and stored in HDPE bottles previously washed according to the above-described procedure for cations. Samples for dissolved organic carbon (DOC) were collected in pyrolysed (550°C) Pyrex test tubes.

Soil pore waters were extracted from humid soil horizons in the field using a Ti pressure device. This titanium vessel has a 50 mm diameter, 150 mm length, and a special thread allowing it to reach $20\,000\text{ kg/cm}^2$ pressure. Depending on saturation state of soil samples, 10 to 50 ml of solution was collected and filtered through a $0.45\text{ }\mu\text{m}$ filter. After each extraction, the vessel and its compartments were thoroughly washed with river water, and afterward, by 100 to 200 ml with distilled water. Before and after fieldwork, blank samples were run by filling the pressure system with MilliQ water at neutral pH and letting it to react for 24 h. No detectable contamination of major and trace elements and DOC was observed.

Major anion concentrations (Cl , SO_4 , F , NO_3 , PO_4) were measured by ion chromatography (HPLC, Dionex ICS 2000) with an uncertainty of 2 %. Calcium, magnesium, sodium, and potassium concentrations were determined using an atomic absorption spectrophotometry (AAS) Perkin-Elmer 5100PC spectrometer with an uncertainty of 2 %. Aqueous silica concentration was determined by standard colorimetry (molybdate blue method) with an uncertainty of 2 % using Technicon automated analyzer. Alkalinity was measured by potentiometric titration with HCl to $\text{pH} = 4.2$ using Gran method with detection limit of 10^{-5} M and an uncertainty of 2 %. DOC was analyzed using a Carbon Total Analyzer (Shimadzu TOC 5000A) with a detection limit of $0.1\text{ }\mu\text{g/l}$ and an uncertainty better than 3 %.

Trace elements were measured without preconcentration by ICP-MS (Elan 6000, Perkin Elmer and 7500ce, Agilent Technologies). Indium and rhenium were used as internal

standards. The international geostandard SLRS-4 (Riverine Water Reference Material for Trace Metals certified by the National Research Council of Canada) was used to check the validity and reproducibility of each analysis. A good agreement between our replicated measurements of SLRS-4 and the certified values was obtained (relative difference < 5 %).

3.2.3. Isotope analysis of surface waters and soils

Strontium and neodymium isotopic ratios were measured by thermal ionization mass spectrometry (TIMS) (Finnigan Mat 261) preceded by chemical separation, involving the dissolution of the sample and chemical extraction of Rb, Sr, Sm and Nd by ion exchange chromatography using three chromatographic materials Sr.Spec, TRU.Spec and Ln.Spec, and HF, HNO₃ and HCl acids in a clean room. Data correction was based on the systematic analysis of the NBS 987 standard for Sr and the La Jolla standard for Nd (i.e., correction for instrumental mass fractionation based on hourly drift at the day of analyses). During this work, the average ⁸⁷Sr/⁸⁶Sr for NBS 987 standard was 0.710250 ± 0.000010 (4 measurements) and 0.511834 ± 0.000006 for ¹⁴³Nd/¹⁴⁴Nd (1 measurement).

4. Results

4.1. Bedrock and soil mineralogy and chemistry

The mineralogy and chemistry of studied rocks are described in **Supplementary Information 2**. Mineral composition of solid material was characterized by structural X-ray analyses of fine (< 0.1 µm, 0.1-2 µm and > 2 µm) and bulk fractions of 10 soil profiles: samples V-4, V-7 (basalts), V-9, V-16 (gneisses), V-15 (peridotites, olivinites) and K-7, K-29 (gneisses), K-14 (olivinites), K-37 (gabbro-norites). Clay mineralogy results presented in this study were obtained on soil samples having enough fine fraction for analysis. However, in boreal podzols, the clay fraction is generally known to be < 5 % (Melkerud et al., 2000;

Mokma et al, 2004; Allen et al., 2001). Although peak intensities in the diffractograms varied somewhat as a function of depth, the $< 2 \mu\text{m}$ fractions from soils developed on basic rocks indicated that quartz (all samples except K-14-C and V-15-O/A), feldspar (all samples except K-14-B₁ and -C and V-15-O/A), amphibole (all samples except K-14-B₁), illite (all samples), chlorite (all samples except K-37-A, V-16-E and -B, V-9-A and V-15-O/A), vermiculite (K-7, K-14, K-37-B₁ and -B₂, V-16-B, V-15), as well as interstratified layers illite/vermiculite (K29-O/A), smectite (K-37-B₁, V-4-E and V-15-O/A) and amorphous phases (K-29, V-16, V-7 and V-9) were the major clay-fraction constituents (**Table 3**). Amorphous aluminosilicates (i. e. imogolite), chlorite, regular interstratified layer mica/vermiculite (25 Å) were found in soil profile K-29 developed on granite-gneiss which is comparable to the clay fraction composition of podzols developed on granite-gneissic rocks in southern Sweden described by Schweda et al. (1991) and in northern Sweden described by Land et al. (1999). Hydrobiotite, a mineral containing regularly interstratified layers of biotite and vermiculite (Sawhney, 1989, Murashkina et al., 2007), was indicated by a peak at 12 Å in felsic soil K-29.

The analysis of the clay fraction in K-14 (**Fig. 2**) indicated the presence of vermiculite (occurrence of a 14.4 Å (7.3 Å) peak on the air-dried pattern, expandable on the ethylene-glycol pattern and collapsed on the heated pattern), illite (10 Å) and amphibole (8.4 Å). The analysis of V-15 peridotite (**Fig. 2A**) showed the presence of both of expandable vermiculite and smectite (vermiculite predominant), and an interstratified layer of illite/vermiculite (23.4 Å). The TEM investigations on the K-14 sample over olivinite from the Kivakka intrusion allowed for acquisition of detailed information on the nature of vermiculite formed in the C horizon of this soil (**Fig. 2B**). These results confirmed the presence of Mg-vermiculite together with chlorite and amphibole which also contained Mg.

Optical and SEM observations on consolidated thin sections of structurally preserved soil samples from different horizons revealed the presence of quartz and feldspar in almost all

studied soil profiles developed on basic rocks: gabbro-norite, olivinite, and peridotite, with the exception of the C horizon of K-14 (soil over olivinite) and the O/A horizon of V-15 (soil over basalt). Zircon was found in soils developed on granite-gneisses (K-7, B horizon; K-29, C horizon, V-16, E horizon). Morphological observations of soils by SEM carried out during this study reveal the presence of etch pits corrosion on the surface of zircon and feldspar (**Fig. 3 A, B**) together with newly-formed matter visible as a coating on quartz, plagioclase and pyroxene surfaces (**Fig. 3 C**). The pH (H₂O) of soils developed on felsic rocks varied between 3.43 and 7.60, and those on basic rocks between 3.82 and 8.74, being the most acid in the surface organic rich soil horizons. The high pH found for V-4 and K-14 soils could be attributed to the mafic nature of the parental rock. Podzolisation process is favoured within low pH environment which is usually the consequence of pedogenesis on acid rocks under deep and acid litter. In this context, the pH (H₂O) measured for the V-16-B and K-8-B samples are problematic (pH is too basic for a podzol type soil). The TOC concentration ranged from 7.7 to 42.1 % wt in organic surface horizons (O/A), and from 0.15 to 3.5 % wt for deeper horizons (E, B and C).

Chemical analysis of soils was performed on bulk fractions (including gravel). Observations of elements concentrations along the soil profiles (not shown) show that all soils developed on felsic rocks exhibited higher content in Si, K (except K-29), Al (except K-7) and Na, and lower content in Ca (except K-29), Fe and Mg with respect to their parent rock. Podzol V-7 developed on basic rocks showed relatively higher content in Si, Al, Na and K than its parent rock similarly to the soils developed on felsic rocks (V-9, K-8, K-29). K-14 and K-37 exhibit low Si, Al and Na content compared to olivinite or gabbro-norite. Higher content in K in the surface horizon compared to the parental rock was observed for all soils except K-14, K-29 and V-15. Almost all soils developed on basic rocks showed lower content in Fe (except K-14) and Mg (except V-9 and V-15) compared to their respective parent rock.

Photos of podzols V-4, K-14 and K-37 developed on basalt, olivinite and gabbro-norite, respectively, and regosol K-29 over gneiss are presented in **Fig. 4**. A diagram of weathering intensity scale (WIS) used to evaluate the chemical index of alteration (Meunier et al., 2013) allows to see how the moraine influences the chemistry of soils (**Fig. 5**). Regardless of the parent rock, the majority of soil samples are located in the “felsic” domain.

4.2. REE distribution pattern

The upper crust (Taylor and McLennan, 1985) normalized rare earth elements (REE) patterns for selected soil samples are plotted in **Fig. 6**. REE patterns of soil horizons are different from those of the corresponding parent rocks. A slightly positive europium anomaly can be observed in the majority of soil horizons and is likely to be related to the presence of feldspar in the soil-rock system. Eu/Eu^* (**Table SI-1**) is calculated using the formula (Condie, 1993):

$$Eu/Eu^* = Eu_N / (Sm_N \cdot Gd_N)^{1/2}$$

where $Gd = (Sm \cdot Tb^2)^{1/3}$. The ratio is within the range 0.87-1.05 for soils on basic rocks for both the Vetreny Belt and the Kivakka intrusion, and 0.88-1.18 and 0.91-1.09 for soils on felsic rocks for the Vetreny Belt and the Kivakka intrusion, respectively. It can be observed that the ratios are quite similar for both felsic and mafic soil-rock systems, again confirming the influence of exterior moraine deposits. This result is further corroborated by extended upper crust (UC) normalized diagrams that include all major and trace elements (**Fig. 7**). The soils of felsic and mafic origin from the Kivakka intrusion site (samples K-7, K-8, K-29 and K-37) are shown in **Fig. 7 A** and for soils from the Vetreny Belt site (samples V-7, V-9, V-16, V-4 and V-15) are shown in **Fig. 7 B**. It can be seen that all soils from the Kivakka intrusion zone exhibited quite similar upper-crust normalized trace elements patterns independent on their parent rock. The soils were generally depleted in most elements compared to the upper

crust: Li, Sc, Mn, Co, Ni, Cu, Zn, As, Rb, Y, Zr, Nb, Mo, Cd (except surface horizons O/A of soils K-7, K-29 and K-37), Sb, Cs, Hf, Ta, W, Tl, Pb, Th, U. For these elements surface horizons O/A appear to be more depleted than the deeper ones. Olivinitic soil K-14 (not shown) exhibited a slightly different pattern, being less depleted in the above mentioned elements relative to the upper crust and enriched in Cr, Co, Zn and Ni, in accord with these elements elevated concentration in the source rocks. For some soil samples a slight enrichment in V (samples K-7-B, V-9-A, V-15-O/A), Cr (K-37 all horizons, V-15-O/A (significantly enriched), V-9-A, V-7-B), Sr (K-29, E and C horizons), Cd (K-7-O/A, K-37-O, V-9, O and A horizons, V-7-E) and Sb (K-7-O/A, K-29-O/A, V-9-O) relative to the upper crust can be observed. The last observation is also true for V-15 sample developed on ultramafic rocks. The soils from the Vetreny Belt zone (**Fig. 7 B**) exhibited similar pattern independent on their parent rocks, and most of them are depleted in Sc, Ti, Co, Ni, Cu, Zn, Ge, Rb, Sr, Y, Zr, Nb, Cs, Hf, Ta, Th, U and significantly in Pb compared to the upper crust. The surface horizons O/A were depleted in V, Cd and Sb. A-horizon of soil V-9 and V-15 were enriched in Sc, V, Cr, Co, Ni, Cd, and all soils were significantly enriched in Tl with respect to the upper crust. Overall, results on TE partitioning in soils corroborate the previous conclusion on the dominant role of glacial deposits on soil chemistry both on mafic and felsic rocks. Taken together, all soils from the Kivakka intrusion and the Vetreny Belt zone exhibit quite similar UC-normalized trace element patterns independent on their parent rock. This confirms the dominant role of glacial deposits on soil chemistry for both mafic and felsic rocks, i.e., the glacial erosion has predetermined the soil development.

4.3. Hydrochemistry of rivers and soil porewaters

Measured pH and temperature, dissolved organic carbon (DOC) concentration, major and some trace elements concentrations (Al, Fe, Sr and Rb), as well as $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios

for river and stagnant mire waters are presented in **Table 2** for both the Kivakka intrusion and the Vetreny Belt zones. The studied waters were essentially of neutral pH varying from 6 to 7.5. However, some surface organic rich waters and bog waters were more acidic with pH decreasing to 4.5-5.5. Bicarbonate ion concentrations ranged from 1.8 to 40.2 mg/l for rivers draining basic rocks and from 8.3 to 80.2 mg/l for rivers draining felsic rocks. In surface wetlands and interstitial waters from soils developed on basalts, the alkalinity ranged from 2.2 to 8.0 and from 1.8 to 29.9 mg/l, respectively. The majority of surficial fluids exhibited high concentrations of dissolved organic carbon between 5 and 40 mg/l.

The composition of the dissolved load of most rivers reflects the weathering of silicate rocks because the total dissolved solids (TDS) expressed as a sum of major inorganic species concentrations (Na, Ca, K, Mg, Al, Fe, H_4SiO_4 , Cl, NO_3 , and SO_4) was low (between 10 and 30 mg/l). These measurements are comparable with previous results on Karelia region (Feoksitov, 2004, Zakharova et al., 2007). Rivers analyzed in this study had an average Si concentration of around 4 mg/l (3.6 ± 0.9 and 4.3 ± 1.3 mg/l for rivers draining felsic and mafic rocks, respectively) which constitutes only 30 % of the TDS. Calcium and sodium were dominant among cations in these waters.

The concentration of major dissolved cations in surface (river and bog) water for both the Vetreny Belt and the Kivakka intrusion zones (average values in $\mu\text{mol/l}$ are given in brackets) followed the order $\text{Ca} (336) > \text{Mg} (116) > \text{Na} (77) > \text{K} (16)$ for waters draining through felsic rocks and $\text{Mg} (95) > \text{Ca} (77) = \text{Na} (77) > \text{K} (7)$ for those draining through mafic rocks. Potassium and sodium concentrations ($16 \mu\text{mol/l}$ and $90 \mu\text{mol/l}$, respectively) were comparable with those reported by Ingri et al. (2005) for a pristine boreal Kalix river draining through a mixed felsic and carbonate-shale environment, whereas calcium content in this study is higher than that of the Kalix river ($149 \mu\text{mol/l}$). We did not detect any systematic difference in Mg concentration between felsic and mafic catchments; concentration varied

from 400 to 8000 $\mu\text{g/l}$ within the Vetreny belt zone and from 100 to 13000 $\mu\text{g/l}$ within the Kivakka intrusion zone. Within the basic rocks catchments, we could not detect any sizeable difference between waters draining through rocks of different composition (gabbro-norites, olivinite, and basalts).

4.4. Radiogenic isotope features

Concentrations of Rb, Sr, Sm and Nd, and $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios for soils from the Vetreny Belt and the Kivakka intrusion are reported in **Table SI-1**. Peculiar feature of soil and water geochemistry in considered zones is large variation of their Sr isotopic composition (**Fig. 8**). For the Kivakka intrusion, soils developed on olivinite (K-14, the deepest horizon) and TTG (K-29) have lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.704) similar to parental rock isotope ratios (Amelin and Semenov, 1996). An opposite tendency is obtained for other soils developed on mafic and felsic rocks (**Fig. 8 A**). For example, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the samples K-37 (0.721-0.726) which was developed on gabbro-norites are similar to those of felsic K-8 (0.721-0.725). These samples are enriched in Rb, and have the same $^{87}\text{Sr}/^{86}\text{Sr}$ ratio as estimated by Land et al. (2000) for podzols developed on Quaternary till of granitic composition in northern Sweden (0.721-0.727). Furthermore, soil horizons B₂ and C of ultramafic sample K-14, and B₂ of mafic sample K-37 have similar pedological characteristics to those of the B horizon of felsic sample K-7, and quite similar in isotope ratio ($^{87}\text{Sr}/^{86}\text{Sr}$ ~0.718 and $^{87}\text{Rb}/^{86}\text{Sr}$ ~0.6). The soils developed on mafic rocks from the Vetreny Belt zone exhibited similar features with $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ isotope ratios higher than their source rocks. This unambiguously suggests strong influence of external (moraine) deposits. Concerning the isotopic composition of surface waters, the results demonstrate two similar tendencies for both sites (**Fig. 8 B**): i) waters show higher Sr isotopic ratios (between 0.715 and 0.730) compared to rocks and rock minerals (between 0.705 and 0.713) within the same

range of $^{87}\text{Rb}/^{86}\text{Sr}$ ratios (from 0 to 0.4), and *ii*) Sr isotope ratios of waters are in the same range as soils (except for soil V-15 from Vetreny Belt site) although soils have higher $^{87}\text{Rb}/^{86}\text{Sr}$ ratios (0.3-0.75) than water (< 0.3). Thus, surface waters have a more radiogenic signature than parental rocks and primary minerals for “basic rock derived” samples.

5. Discussion

5.1. Moraine influence over the full depth of soil profile

5.1.1. Major elements

The occurrence of corroded zircon and feldspar and the evidence of clay mineral formation in those soils witness similar weathering processes on all types of parental rock. Etch-pitting of zircon is usually related to intense weathering processes, generally in tropical environment (e. g. Oliva et al., 1999). However, the lack of kaolinite neoformation and the persistence of amphibole and plagioclase feldspar in soils suggest not very intense weathering processes, consistent with the beginning of pedogenesis about 10 Ky ago. Our mineralogical observations of secondary phases are consistent with the presence of hydrobiotite, amorphous phases, smectite and K-feldspar over nepheline syenite in horizons C and B₂ as well as quartz and plagioclase in horizons B₁ and E described in mountainous tundra soils of northwestern Russia (Lesovaya et al., 2008). These results are also compatible with the clay fraction composition of soils developed on glacial moraines in Finland (gneissic moraine material) (Melkerud et al., 2000; Mokma et al., 2004) which includes quartz, plagioclase, K-feldspar, amphibole, chlorite, illite, mixed layer illite/vermiculite, and allophanes. Observed mixed layer chlorite/vermiculite is reported as a product of degradation of chlorite.

Classically, element depletion or enrichment in soils samples compared to respective unaltered rocks at the soil profile scale (i.e., mass balance approach) is estimated via element ratios with invariant low-mobility elements (i. e. Zr, Ti, Al, Th) in soils and rocks (**Table SI-**

1). Theoretical concentrations of major elements in soil profiles were systematically higher compared to the parental rock for Na and/or K except for the B₁ and C-horizons in samples K-14 (soil over olivinite, Kivakka intrusion) and V-15 (soil over peridotite, Vetreny Belt). Moreover, the Zr/Ti ratio was not constant along the soil profiles as we observed a depletion in Zr in O and A horizons and slight enrichment in B horizons. This may suggest that Zr or Ti were not initially homogeneously distributed in soils or that Ti is not invariant in these profiles. Potential Zr mobility in soils and the difficulty of using Zr as refractory element for mass balance calculations are widely known (see recent work in Southern Spain, Ameijeiras-Marino et al., 2017). Similar results were observed when using Al and Th as invariants. One reason for this discrepancy can be the unusually high mobility of tetravalent elements in the form of large-size organo-mineral ferric colloids whose presence is unambiguously demonstrated in surficial waters of the Karelian zone (Pokrovsky and Schott, 2002; Vasyukova et al., 2010). Using a CDF (chemical depletion fraction corresponding to the ratio of chemical erosion rates to mineral supply rates) and chemical depletion fractions of individual elements (Brimhall et al., 2001; Riebe et al., 2001 and 2004; Ferrier et al., 2016) provide a more comprehensive approach of the chemical differentiation of the soil relative to its parent material. In particular, CDF calculations allow to take into consideration external element supply to the soils. Following Riebe et al. (2001, 2004), we calculated:

$$\text{CDF} = 1 - ([\text{Ti}]_{\text{rock}} / [\text{Ti}]_{\text{soil}}) \text{ for the entire soil}$$

$$\text{CDF}_x = 1 - ([\text{X}]_{\text{soil}} / [\text{X}]_{\text{rock}}) \times ([\text{Ti}]_{\text{rock}} / [\text{Ti}]_{\text{soil}}) \text{ for individual element X}$$

The CDF values using Ti as an invariant element (**Table 4**) showed important discrepancies (i.e., values from 2 to -1670%) between different soil samples, including even the samples taken within the same soil profile (K-8 and V-9 soil samples). These differences are not linked to the nature of parental rock (i.e., mafic vs felsic). Positive CDF values in samples K-7, K-14 and K-37 can be related to chemical losses from the parental material whereas

negative values in K-29, V-4, V-7 and V-16 can be attributed to fresh mineral supply to the regolith. In soils where chemical dedudation seems to occur, positive CDF values should decrease or remain constant from surface to depth. This was only observed in K-7 and K-37 soils. Thus, even for soil with positive CDF, the pathway and rate of chemical weathering cannot be constrained. When chemical depletion fraction of individual element is considered (**Table 4**), only K-14 B₁ and C horizons samples show positive values for all considered element. Chemical depletion fraction of individual element confirm the relative enrichment of soil samples in K and to a lesser extend in Na compared to the parental rocks. Some samples, however, do not exhibit relative enrichment in K (K-29 samples, V-9 A and V-15 O/A horizon samples) or in Na (K-8 E, K-37 O, K-37 A, V-9 O, V-9 A and V-15 O/A horizon samples) suggesting diverse origin of chemical supply to the soils. For example, K-29 soil samples developed over felsic formation (i.e., granite/gneiss) showed negative CDF values in Na, Ca, Al and Si. The enrichments in Si and Al are difficult to interpret as they mainly occur in horizons presenting spodic properties that can result from element mobilisation within the soil profile.

Another widely used proxy for chemical weathering intensity of source rocks for soils and sediments is Chemical Index of Alteration (CIA; Nesbitt and Young, 1982; Fedo et al., 1995, Li and Yang, 2010). It is calculated using the molar proportion of major elements, as follows:

$$CIA = [Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O)] \times 100$$

where CaO* used in the CIA calculation refers to CaO from the silicate fraction exclusively. Basic rocks exhibit average CIA values (42 and 36 for Kivakka layered intrusion and Vetreny Belt paleorift respectively) which are lower than the CIA of felsic rocks (CIA value of archaean granite ~50). It can be observed that the CIA of soils is not always higher than that of their respective parent rocks (**Table 4**). The ratio $CIA_{\text{soil sample}}/CIA_{\text{parent rock}}$ is considered as a

proxy of the “weathering degree” of a soil. Some samples (V-15, V-9, K-8-C, all the K-29 samples) show CIA_s/CIA_r values lower than 1. Since the CIA calculation involves Al (thought to be rather mobile during podzolisation) and K (a nutrient highly recycled by vegetation), several hypotheses can explain this CIA value: 1) the loss of Al during weathering of K-feldspars and downward migration due to podzolisation occurring mainly in E horizon; 2) the accumulation of K from buried organic matter in the form of plant litter in the uppermost organic-rich soil horizons, and 3) the input of K, Al, Ca, and Na from allochthonous sources.

Al loss during podzolisation usually affects the O, A and E horizons (Melkerud et al., 2000; Olsson et al., 2000; Giesler et al., 2000); K incorporation may affect O horizon and the effect of addition of allochthonous material depends on its origin (e. g. aeolian, morainic) and composition. Incorporation of allochthonous material may actually lead to a “dilution” effect thus underestimating the element content in the soil profile. As a result, even at zero level of chemical weathering intensity, the presence of moraine or aeolian material can lead to an under- or overestimation of the CIA depending on the chemical composition of the mineral supply. Except in a few samples mentioned above, most soils developed on mafic rocks showed $CIA_s/CIA_r > 1$ which is higher than that in soils over felsic formation ($CIA_s/CIA_r \sim 1$). However, the dilution effect of the moraine was more pronounced for basic rocks compared to acidic rocks because of the felsic dominant nature of the moraine.

Mineralogical studies performed on soils samples show the presence of ubiquitous quartz (and in some soils, zircon) independent on the nature of the parental rocks. The size of quartz grains varied from 10 to 450 μm and from 50 to 200 μm in soils developed on mafic and felsic rocks, respectively, which precluded an aeolian origin of these quartz grains. In contrast, quaternary (Pleistocene) deposits observed even in the deepest horizons of some soil profiles (**Fig. 4 E**) confirm a strong moraine influence in this region. This moraine altered significantly the chemistry of soils as it can be seen on the WIS diagram (**Fig. 5, Table 4**) that

take into account a silica component (Meunier et al., 2013). All studied rocks fall in their respective “domain” within the WIS diagram. On the opposite, soils samples, whatever their parental rock, fall in the “felsic domain”, with the exception of the V-7 C, K-14, V-15 and V-9 soils samples. Only the K-14 B1 and K-14 C samples are plotted close to the parental olivenite suggesting a poor influence of allochthonous morainic material in K-14 soil pedogenesis. In the felsic domain, TTG and glacial till (Lunkka et al., 2013) are chemically similar with silica content lower than soils samples. This is coherent with chemical weathering processes in cold environment which involve relative enrichment in silica (quartz preservation) in comparison with the alkaline earth elements (M^+ pole; $Na^+ + K^+ + 2Ca^{2+}$) or the divalent metallic elements (R^{2+} pole; $Mg^{2+} + Fe^{2+} + Mn^{2+}$) that are lost from the soil during pedogenesis. This trend is particularly pronounced when comparing E and B horizons of podzolic soils on the WIS diagram. E horizons are systematically closer to the 4Si pole than the B horizon. Such results suggest that, even if a strong morainic influence has completely modified the mineralogical and chemical nature of the initial regolith, the soil forming processes such as podzolisation occurring within these soils are similar and consistent among different sites.

5.1.2. REE fractionation between rocks and soils

Five horizons of a soil developed on gabbro-norites (sample K-37 from the Kivakka intrusion, **Fig. 6 A**) show enrichment in light rare earth elements (LREE) and depletion in heavy rare earth elements (HREE) relative to the gabbro-norite. Enrichment in LREE was also observed by Öhlander et al. (1996) in B-horizons of spodosols developed on felsic till in northern Sweden, whereas E-horizons were depleted in all REE, with LREE being more depleted than HREE. According to Öhlander et al. (1996), this secondary enrichment in B-horizons could be caused by adsorption on secondary oxy-hydroxides, on clay minerals or

organic material, or by the precipitation of secondary LREE enriched phosphates. Note the higher affinity of LREE to adsorb on oxy(hydr)oxides and the tendency of HREE to form more stable dissolved complexes than LREE in solution (Bau, 1999) is in agreement with these tendencies.

Olivinite rock is enriched in HREE, and sample K-14 B₂ from the Kivakka intrusion (**Fig. 6 B**) is enriched in all REE relative to olivinite for all horizons of the soil profile. On the contrary, soils developed on felsic rocks (samples K-7, K-8, K-29 from Kivakka intrusion, **Fig. 6 C**) have inverted REE concentrations with respect to parental granite, all horizons are depleted in REE relative to the source rock. The REE patterns of soils developed both on mafic and felsic rocks in the Vetreny Belt zone (**Fig. 6 D**) demonstrate that soils developed on basalt (samples V-4 and V-7) are depleted in REE with respect to parental rock with the exception of the B horizon of V-7 which is slightly enriched in LREE. Soils over felsic rock are also more significantly depleted in all REE relative to the source TTG. However, it can be seen that patterns of soils with different origins (mafic or felsic) are quite similar. This is further illustrated in **Fig. 6 E** where the E or B horizons of different soils developed on both felsic (K-7, K-8, K-29) and mafic (K-14, K-37) rocks are plotted. It demonstrates that the REE fractionation in intermediate horizons in all studied soils is identical regardless of the underlying rock. This result is in agreement with observations of Lesovaya et al. (2008) on podzols and podzolized podburs on mafic substrates under the influence of glacial moraine deposits in mountainous taiga areas in northwestern Russia. According to these authors, the mineralogical effect of the admixture of gneiss-derived material is, in general, most pronounced in the E horizon.

5.2. Actual weathering processes: waters versus soils and rocks

A binary logarithmic diagram of the molar Ca/Na versus Mg/Na ratios in rocks, soils and waters, including atmospheric precipitation shows that the Ca/Na ratio ranges from 0.2 to 8.6 and 0.25 to 5.8 for soils and waters, respectively (**Fig. 9**). The Mg/Na ratio varies between 0.15 and 8.9 for waters, and between 0.1 and 1.9 for soils; the highest ratio of 76.5 and 214.3 are for soil K-14 on olivinite (B₁ and C horizons, respectively). There is a good correlation between Ca/Na and Mg/Na ratios in soils and rocks, and between surface waters and rocks. The majority of samples from the Kivakka intrusion and the Vetreny Belt, exempting soils K-29 (horizon E) and K-14 (horizons B₁ and C) which drop out of the tendency, are located on the mixing line between silicate and carbonate end-members although no clear evidence of carbonate phases was previously described for neither rocks nor soils and no carbonate mineral was found within the resolution of XRD analysis of soils.

Lower Ca/Na and Mg/Na ratio for soils compared to rocks is consistent with on-going chemical weathering, as calcium-rich phases usually weather more rapidly than sodium-rich phases in silicate environments. In this regard, the addition of moraine material enriched in Na (Na-K feldspar) can also explain this tendency. Lesovaya et al. (2008) observed the presence of moraine admixtures in mafic rock-soil systems, expressed in the lower content of calcium in the middle taiga soils of Karelia which could be due to the admixture of stable K-Na feldspars.

Stream waters are known to have higher Ca/Na molar ratio than rocks and soils and should exhibit lower Ca/Na ratio compared to parental rocks (Gaillardet et al., 1999; Oliva et al., 2004). We observe different tendencies of water composition: surface waters are situated either in the same region or are enriched in Ca or Mg compared to soils in the case of the Vetreny Belt rock-soil-water system. For the Kivakka intrusion system the surface fluids are located between the soil and rock reservoirs reflecting preferential mobilisation of sodium

relative to calcium or magnesium in these surface waters as compared to rocks. The waters from the Vetreny Belt mafic rocks exhibit higher Mg/Na and lower Ca/Na ratios compared to the Kivakka basic massif and surrounding felsic rocks, which is in agreement with higher Mg concentrations in basalts of the Vetreny Belt (up to 20-25 % MgO in spinifex-like structures, see Kulikov et al., 2005).

Unexpectedly, surface waters draining felsic environments show higher Ca/Na and Mg/Na molar ratios than waters draining mafic rocks. This relative enrichment in Na with respect to Ca and Mg in rivers from mafic watersheds compared to felsic watershed may be explained by a higher mobility of sodium compared to Ca and Mg during the weathering process and the retention of Mg and Ca during secondary phases forming. It is possible that Ca and Mg, unlike Na, participate in secondary mineral formation such as Mg-vermiculite. Some Ca and Mg rich phases (i. e. CaMg-amphibole) can also weather less rapidly than Na-rich feldspar (Salminen et al., 2008). Soil K-14 which is over olivinite (B and C horizons) exhibited a clear tendency of enrichment in Mg and Ca compared to Na during basic rock weathering. This is consistent with the presence of Mg-vermiculite and CaMg-amphibole in the clay fraction. The persistence of Ca-amphibole in such soils has been also observed by Lesovaya et al. (2008).

Consistent with these chemical and mineralogical observations, the radiogenic isotopes demonstrate two features of the water-soil-rock system development in NW Russia (**Fig. 8**): (1) During different stages of weathering, easily weatherable and less radiogenic minerals (secondary clays, carbonates) were strongly consumed throughout the full depth of examined soil profile. This provided a more radiogenic Sr isotopic signature to most soils developed on mafic rocks compared to that of the parent rocks which was especially pronounced in the surface horizons. For both the Kivakka intrusion and the Vetreny Belt, we observe a shift of $^{87}\text{Sr}/^{86}\text{Sr}$ from ~ 0.705 (rocks) to 0.715-0.725 (soils). The same behaviour

was reported for soils developed over basalts in Central Siberia (Bagard et al., 2013). Second, all the granitic moraine in Karelian region had a more radiogenic signature than the studied bedrocks. Isotope signatures of waters draining through both felsic and mafic zone reflect the weathering of more radiogenic minerals. However, these radiogenic signatures are lower than that reported by Land et al. (2000) for stream waters (~0.74) draining felsic rocks in northern Sweden within the Kalix river watershed.

5.3. Chemical weathering rates

In general, the composition of surface waters does not reflect a purely felsic or mafic source being similar in all waters, except for one Mg-rich surface water draining through olivinite environment of the Kivakka intrusion (sample K-13-w). The surface waters draining through both Kivakka and Vetreny Belt region are strongly oversaturated with respect to $\text{Al}(\text{OH})_3$, boehmite, gibbsite, halloysite, imogolite, kaolinite, ferrihydrite (factor 10 to 10^6), and undersaturated with respect to amorphous silica, and close to saturation with quartz. Apparently, the amorphous, organic-rich Al and Fe oxyhydroxides and silicates constitute a major part of secondary phases in soils as is well known for boreal zone (Lundström et al., 2000, Giesler et al., 2000). One particular feature in soil K-14 is the occurrence of Mg-vermiculite and a high pH. Processes usually occurring in podzolic soils are rock dismantling, Al- and Fe-organic complex formation, organic matter modification, oxidation of iron bearing primary phases, and amorphous alumino-silicate precipitation. However, the podzolation process is known to rarely produce any clay mineral formation and clays are relatively absent (Mokma et al., 2004).

Only the K-14-C soil sample was not affected by moraine deposit, and thus, it can be used in calculation of weathering rates of basic rocks. Our results give a long term TDS weathering rate of 1184 eq/ha/yr for olivinite rock, which is 4 times higher than the long term

base cation flux (360 eq/ha/yr) and about 2 times higher than the actual TDS weathering rate (~700 eq/ha/yr) estimated by Land et al. (1999) for granitic till in northern Sweden. This value corresponds to a long term weathering rate of ~1.5 t/km²/yr which is lower than the present day weathering rate estimated by Zakharova et al. (2007) and Pokrovsky et al. (2005) for Karelian and Siberian mafic rocks (2.3 and 5-6 t/km²/y, respectively) but comparable with chemical denudation rates of Canadian granites (0.35 to 1.55 t/km²/y for Slave Province vs Grenville, Millot et al., 2002). Calculation of weathering fluxes were conducted for A and B₁ horizons and give values of 364 eq/ha/yr and 148 eq/ha/yr, respectively, which are consistent with fluxes reported by Land et al. (1999) for the granitic till, and for podzol soils covered by Norway spruce in Sweden (344 eq/ha/yr for Ca+Mg+Na+K, Simonsson et al., 2015). These values are sizebly lower than the base cations release rate, calculated for similar environmental context using various mineral dissolution models (1400-2700 eq/ha/yr, Erlandsson et al., 2016).

Results of the present study demonstrate that the weathering rates of ultramafic rocks are higher than those of the felsic till, but dominant moraine deposits in this region hide the true magnitude of weathering processes. The dominant mechanism responsible for slowing the rates of mafic rock weathering could be retention of Mg and Ca in soil are likely due to precipitation of secondary phases such as Mg-vermiculite or adsorption on mineral, organic, or organo-mineral phases.

6. Conclusions

A multidisciplinary study of mafic rocks weathering in the region affected by glacial moraine deposits (northwestern Russia) demonstrated the following:

(1) Traces of chemical corrosion on the surface of zircons and feldspars along with the presence of new-formed amorphous matter on the surface of quartz, plagioclases and

pyroxenes are evidence of similar weathering processes on all types of parental rock. However, the lack of kaolinite neoformation and the persistence of amphibole and plagioclase feldspar in soils suggest not very intense weathering processes, in accordance with a start of pedogenesis about 10 Ky ago.

(2) The presence of quartz and zircon in soils developed on basic rocks, similarity of REE patterns of intermediate and deep soil horizons both for felsic and mafic rocks, and the isotopic signature of soils on gabbro-norite and olivinite similar to that of granodiorites raise a question of the polycyclic nature of these soils (soil developed on fragments of already pre-existing soil), and assume their “contamination” with exterior deposits such as granitic moraine.

(3) The relative enrichment in Na with respect to Ca and Mg in rivers from both felsic and mafic watersheds suggests a contribution from other sources than primary silicate weathering reactions. We suggest that either Mg-vermiculite and Ca, Mg-amphibole formation in soils limits Ca and Mg release to surface waters, or that there are highly weatherable Ca- and Mg-rich minerals present in felsic rocks. These specific features should be taken into account in estimation of mafic rocks weathering rates and calculations of atmospheric CO₂ consumption for weathering in such a particular environment.

(4) The radiogenic isotopes of the water-soil-rock system development in NW Russia demonstrated *i*) preferential removal of easily weatherable and less radiogenic minerals throughout the full depth of soil profile, and *ii*) more radiogenic signature of the granitic moraine compared to mafic and felsic bedrocks.

(5) In the cold subarctic climate, even thin deposits of glacial till moraine are capable of “protecting” mafic rocks from direct chemical weathering. As a result, over 10 000-15 000 years of exposure after the last glaciation, full weathering soil profiles on basic rocks could not be established.

(6) The weathering rates of ultramafic rocks are higher than those from felsic till, but widespread moraine depositions in this region hide the magnitude of weathering processes. These findings may have broad applications for reconstructing paleo environments and quantifying the true capacity of igneous silicate rocks to absorb CO₂ during weathering in high latitude regions.

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References

- AFNOR, 1996. Qualité des sols. Recueil de normes Françaises, Association Française de Normalisation, Paris.
- Akselsson, C., Holmqvist, J., Kurz, D., Sverdrup, H., 2006. Relations between elemental content in till, mineralogy of till and bedrock mineralogy in the province of Småland, southern Sweden. *Geoderma* 136, 643-659.
- Alapieti, T., 1982. The Koillismaa layered igneous complex, Finland: its structure, mineralogy and geochemistry, with emphasis on the distribution of chromium. *Bull. Geol. Surv. Finl.* 319, 116.
- Allen, C., Darmody, R., Thorn, C., Dixon, J., Schlyter, P., 2001. Clay mineralogy, chemical weathering and landscape evolution in Arctic-Alpine Sweden. *Geoderma* 99, 277-294.
- Amelin, Y., Semenov, V., 1990. On the age and sources of magmas for the early Proterozoic layered intrusions of Karelia (abstracts of contributions). *Isotopic dating of endogenic ore associations*, Tbilisi, 40-42.
- Amelin, Y.V., Semenov, V.S., 1990. Age and magma source of the early Paleoproterozoic layered intrusions of Karelia (in Russian). In *Proceedings of all-USSR conference "Isotope dating of endogenous ore formations"*, XXIV session, Tbilisi, November 12-18, 1990, 40-42.
- Amelin, Y.V., Heaman, L., Semenov, V., 1995. U-Pb geochronology of layered mafic intrusions in the eastern Baltic Shield: implications for the timing and duration of Paleoproterozoic continental rifting. *Precambrian Res.* 75, 31-46.
- Amelin, Y.V., Semenov, V.S., 1996. Nd and Sr isotopic geochemistry of mafic layered intrusions in the eastern Baltic shield: implications for the evolution of Paleoproterozoic continental mafic magmas. *Contrib. Mineral. Petrol.* 124, 255-272.
- Ameijeiras-Marino, Y., Opfergelt, S., Schoonejans, J., Vanacker, V., Sonnet, P., de Jong, J., Delmelle, P., 2017. Impact of low denudation rates on soil chemical weathering intensity: A multiproxy approach. *Chem. Geol.* 456, 72-84.
- Anderson, H., Berrow, M., Farmer, V., Hepburn, A., Russell, J., Walker, A., 1982. A reassessment of podzol formation processes. *J. Soil Sci.* 33, 125-136.
- Andersson, P. S., Porcelli, D., Gustafsson, O., Ingri, J., Wasserburg, G. J., 2001. The importance of colloids for the behavior of uranium isotopes in the low-salinity zone of

- a stable estuary. *Geochim. Cosmochim. Acta* 65(1), 13–25.
- Andersson, K., Dahlqvist, R., Turner, D., Stolpe, B., Larsson, T., Ingri, J., Andersson, P., 2006. Colloidal rare earth elements in a boreal river: Changing sources and distributions during the spring flood. *Geochim. Cosmochim. Acta* 70, 3261–3274.
- Andrews, L.C., Catania, G.A., Hoffman, M.J., Gulley, J.D., Lüthi, M.P., Ryser, C., Hawley, R.L., Neumann, T.A., 2014. Direct observations of evolving subglacial drainage beneath the Greenland Ice Sheet. *Nature* 514, 80–83.
- Bagard M.-L., Schmitt A.-D., Chabaux F., Pokrovsky O.S., Viers J., Stille P., Labolle F., Prokushkin A.S. (2013) Biogeochemistry of stable Ca and radiogenic Sr isotopes in larch-covered permafrost-dominated watersheds of Central Siberia. *Geochimica Cosmochimica Acta*, 114, 169–187.
- Balagizi, C., Darchambeau, F., Bouillon, S., Yalire, M., Lambert, T., Borges, A., 2015. River geochemistry, chemical weathering, and atmospheric CO₂ consumption rates in the Virunga Volcanic Province (East Africa). *G³*, 16, 2637–2660.
- Balashov, Y.A., Bayanova, T.B., Mitrofanov, F. P., 1993. Isotope data on the age and genesis of layered basic-ultrabasic intrusions in the Kola Peninsula and northern Karelia, northeastern Baltic Shield. *Precambrian Res.* 64, 197–205.
- Barkov, A., Gannibal, L., Ryungenen, G., Balashov, Y., 1991. Zircon dating of the Kivakka layered massif, Northern Karelia. Abstracts of papers. All-USSR seminar on methods of isotopic geology, Zvenigorod, 21–25 October 1991, St. Petersburg, 21–23.
- Bau, M., 1999. Scavenging of dissolved yttrium and rare earths by precipitating iron oxyhydroxide: Experimental evidence for Ce oxidation, Y-Ho fractionation, and lanthanide tetrad effect. *Geochim. Cosmochim. Acta* 63, 67–77.
- Berner, R. A., Lasaga, A. C., Garrels, R. M., 1983. The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. *Am. J. Sci.* 283, 641–683.
- Berner, R., 1992. Weathering, plants, and the long-term carbon cycle. *Geochim. Cosmochim. Acta* 56(8), 3225–3231.
- Berner, R., 1995. Chemical weathering and its effect on atmospheric CO₂ and climate. *Reviews in Mineralogy and Geochemistry* 31(1), 565–583.
- Berner, R., Caldeira, K., 1997. The need for mass balance and feedback in the geochemical carbon cycle. *Geology* 25, 955–956.
- Bibikova, E. V., Samsonov, A. V., Petrova, A. Y., Kirnozova, T. I., 2005. The Archean geochronology of Western Karelia. *Stratigraphy and Geological Correlation* 13(5), 459–475.
- Boeglin, J., Probst, J., 1998. Physical and chemical weathering rates and CO₂ consumption in a tropical lateritic environment: the upper Niger basin. *Chem. Geol.* 148(3–4), 137–156.
- Brady, P.V., 1991. The Effect of silicate weathering on global temperature and atmospheric CO₂. *Journal of Geophysical Research* 96(B11), 18101–18106.
- Breemen van, N., Buurman, P., 1998. *Soil Formation*, 245–270. Kluwer Academic Publishers, Dordrecht, Boston.
- Brimhall, G. H., Lewis, C. J., Ford, C., Bratt, J., Taylor, G., Warin, O., 1991. Quantitative geochemical approach to pedogenesis: importance of parent material reduction, volumetric expansion, and eolian influx in lateritization. *Geoderma* 51, 51–91.
- Buurman, P., 1984. *Podzols: Temperate regions* (Van Nostand Reinhold soil science series). Van Nostand Reinhold, New York.
- Buurman, P., Jongmans, A., 2005. Podzolisation and soil organic matter dynamics. *Geoderma* 125(1–2), 71–83.
- Bychkova, Y.V., 2003. Structural patterns of contrasting rhythmic layering of Kivakka intrusion. PhD thesis, Moscow State University.
- Bychkova, Y., Koptev-Dvornikov, E., 2004. Rhythmic layering of Kivakka type: geology,

- petrology, petrochemistry, hypothesis of formation (in Russian). *Petrology* 12(3), 281-302.
- Bychkova, Y. V., Koptev-Dvornikov, E. V., Kononkova, N. N., Kameneva, E. E., 2007. Composition of rock-forming minerals in the Kivakka layered massif, Northern Karelia, and systematic variations in the chemistries of minerals in the rhythmic layering subzone. *Geochemistry International* 45(2), 131–151.
- Caritat de, P., Reimann, C., Bogatyrev, I., Chekushin, V., Finne, T. E., Halleraker, J. H., Kashulina, G., Niskavaara, H., Pavlov, V., Ayras, M., 2001. Regional distribution of Al, B, Ba, Ca, K, La, Mg, Mn, Na, P, Rb, Si, Sr, Th, U and Y in terrestrial moss within a 188,000 km² area of the central Barents region: influence of geology, seaspray and human activity. *Appl. Geochem.* 16, 137-159.
- Condie, K. C., 1993. Chemical composition and evolution of the upper continental crust: Contrasting results from surface samples and shales. *Chem. Geol.* 104(1-4), 1-37.
- Cornu, S., Lucas, Y., Lebon, E., Ambrosi, J. P., Luizão, F., Rouiller, J., Bonnay, M., Neal, C., 1999. Evidence of titanium mobility in soil profiles, Manaus, central Amazonia. *Geoderma* 91(3-4), 281-295.
- Courchesne, F., Hendershot, W., 1997. Essai. La Genèse des podzols', *Geogr. Phys. Quarter.* 51, 235-250.
- Dahlqvist, R., Benedetti, M. F., Andersson, K., Turner, D., Larsson, T., Stolpe, B., Ingri, J., 2004. Association of calcium with colloidal particles and speciation of calcium in the Kalix and Amazon rivers. *Geochim. Cosmochim. Acta* 68(20), 4059-4075.
- Dahlqvist, R., Andersson, K., Ingri, J., Larsson, T., Stolpe, B., Turner, D., 2007. Temporal variations of colloidal carrier phases and associated trace elements in a boreal river. *Geochim. Cosmochim. Acta* 71, 5339-5354.
- D'Amico, M., Julitta, F., Previtali, F., Cantelli, D., 2008. Podzolization over ophiolitic materials in the western Alps (Natural Park of Mont Avic, Aosta Valley, Italy). *Geoderma* 146, 129-137.
- Debon, F., Enrique, P., Autran, A., 1995. Magmatisme Hercynien. Synthèse géologique et géophysique des Pyrenees. Edt BRGM 1, Cycle Hercynien (eds. A. Barnolas and J. C. Chiron), 361-499.
- DePaolo, D., Wasserburg, G., 1976. Inferences about magma sources and mantle structure from variations of ¹⁴³Nd/¹⁴⁴Nd. *Geophys. Res. Lett.* 3, 249-252.
- DePaolo, D. J., 1981. Neodymium isotopes in the Colorado Front Range and crust-mantle evolution in the Proterozoic. *Nature* 291, 193-196.
- DePaolo, D., 1988. Neodymium isotope geochemistry: an introduction. Springer-Verlag, New York, p. 187.
- Dessert, C., Dupré, B., Francois, L. M., Schott, J., Gaillardet, J., Chakrapani, G., Bajpai, S., 2001. Erosion of Deccan Traps determined by river geochemistry: impact on the global climate and the ⁸⁷Sr/⁸⁶Sr ratio of seawater. *Earth Planet. Sci. Lett.* 188, 459-474.
- Dessert, C., Dupré, B., Gaillardet, J., François, L. M., Allègre, C. J., 2003. Basalt weathering laws and the impact of basalt weathering on the global carbon cycle. *Chem. Geol.* 202, 257-273.
- Dessert, C., Lajeunesse, E., Lloret, E., Clergue, C., Crispi, O., Gorge, C., Quidelleur, X., 2015. Controls on chemical weathering on a mountainous volcanic tropical island: Guadeloupe (French West Indies). *Geochimica et Cosmochimica Acta* 171, Pages 216-237.
- Deuerling, K.M., Martin, J.B., Martin, E.E., Scribner, C.A., 2018. Hydrologic exchange and chemical weathering in a proglacial watershed near Kangerlussuaq, west Greenland. *J. Hydrol.* 556, 220-232.
- Dokuchaev, V., 1880. On podzol (in Russian). *Trudy Volnogo ekonomicheskogo obschestva* 1(2), 142-150.

- Dupré, B., Gaillardet, J., Rousseau, D., Allègre, C. J., 1996. Major and trace elements of river-borne material: The Congo Basin. *Geochim. Cosmochim. Acta* 60(8), 1301-1321.
- Dupré, B., Dessert, C., Oliva, P., Godderis, Y., Viers, J., Francois, L., Millot, R., Gaillardet, J., 2003. Rivers, chemical weathering and Earth's climate. *C. R. Geoscience* 335, 1141-1160.
- Eiriksdottir, E., Gislason, S., and Oelkers, E., 2013. Does temperature or runoff control the feedback between chemical denudation and climate? Insights from NE Iceland: *Geochimica et Cosmochimica Acta*, v. 107, p. 65–81
- Eiriksdottir, E.S., Gislason, S.R., Oelkers, E.H., 2015. Direct evidence of the feedback between climate and nutrient, major, and trace element transport to the oceans. *Geochim. Cosmochim. Acta* 166, 249-266.
- Erlandsson, M., Oelkers, E.H., Bishop, K., Sverdrup, H., Belyazid, S., Ledesma, J.L.J., Köhler, S.J., 2016. Spatial and temporal variations of base cation release from chemical weathering on a hillslope scale. *Chemical Geol.* 441, 1-13.
- Fedo, C. M., Nesbitt, H. W., Young, G. M., 1995. Unraveling the effects of potassium metasomatism in sedimentary rocks and paleosols, with implications for paleoweathering conditions and provenance. *Geology* 23(10), 921-924.
- Feoktistov, V. M., 2004. Water chemical composition of Karelian rivers and their dissolved chemical discharge into the White Sea. *Water Resour.* 31(6), 631-638.
- Ferrier, K. L., Riebe, C. S., Hahm, W. J., 2016. Testing for supply-limited and kinetic-limited chemical erosion in field measurements of regolith production and chemical depletion, *Geochem. Geophys. Geosyst.* 17, 2270–2285.
- Foster, G.L., Vance, D., 2006. Negligible glacial-interglacial variation in continental chemical weathering rates. *Nature* 444, 918-921.
- Gaillardet, J., Dupré, B., Louvat, P., Allègre, C., 1999. Global silicate weathering and CO₂ consumption rates deduced from the chemistry of large rivers. *Chem. Geol.* 159, 3-30.
- Gaillardet, J., Rad, S., Rive, K., Louvat, P., Gorge, C., Allègre, C.J., Lajeunesse, E., 2011. Orography-driven chemical denudation in the Lesser Antilles: Evidence for a new feed-back mechanism stabilizing atmospheric CO₂. *American Journal of Science* 311, 851-894.
- Giesler, R., Ilvesniemi, H., Nyberg, L., van Hees, P., Starr, M., Bishop, K., Kareinen, T., Lundström, U., 2000. Distribution and mobilization of Al, Fe and Si in three podzolic soil profiles in relation to the humus layer. *Geoderma* 94, 249-263.
- Gislason, S. R., Arnorsson, S., Armannsson, H., 1996. Chemical weathering of basalt in Southwest Iceland, effects of runoff, age of rocks and vegetative/glacial cover. *American Journal of Science* 296, 837-907.
- Goldstein, S., O'Nions, R., Hamilton, P. 1984. A Sm-Nd study of atmospheric dusts and particulates from major river system. *Earth Planet. Sci. Lett.* 70, 221-236.
- Grard, A., François, L., Dessert, C., Dupré, B., Goddérès, Y., 2005. Basaltic volcanism and mass extinction at the Permo-Triassic boundary: Environmental impact and modeling of the global carbon cycle. *Earth Planet. Sci. Lett.* 234(1-2), 207-221.
- Hättestrand, C. (1997), Ribbed moraines in Sweden – distribution pattern and palaeoglaciological implications, *Sedimentary Geology* 111, 41-56.
- Hawley, S.M., Pogge von Strandmann, P.A.E., Burton, K.W., Williams, H.M., Gislason, S.R., 2017. Continental weathering and terrestrial (oxyhydr)oxide export: Comparing glacial and non-glacial catchments in Iceland. *Chem. Geol.* 462, 55-66.
- Hindshaw, R.S., Rickli, J.R., Leuthold, J., Wadham, J., Bourdon, B., 2014. Identifying weathering sources and processes in an outlet glacier of the Greenland Ice Sheet using Ca and Sr isotope ratios. *Geochim. Cosmochim. Acta* 145, 50-71.
- Horton, T., Chamberlain, C.P., Fantle, M., Blum, J., 1999. Chemical weathering and

- lithologic controls of water chemistry in a high-elevation river system: Clark's Fork of the Yellowstone river, Wyoming and Montana. *Water Resour. Res.*, 35, 1643-1655.
- Ibarra, D., Caves, J., Moon, S., Thomas, D., Hartmann, J., Page Chamberlain, C., Maher, K., 2016. Differential weathering of basaltic and granitic catchments from concentration–discharge relationships. *Geochimica et Cosmochimica Acta* 190, 265-293.
- Ingri, J., Widerlund, A., Land, M., Gustafsson, O., Andersson, P. S., Öhlander, B., 2000. Temporal variations in the fractionation of the rare earth elements in a boreal river, the role of colloidal particles. *Chem. Geol.* 166, 23-45.
- Ingri, J., Widerlund, A., Land, M., 2005. Geochemistry of major elements in a pristine boreal river system, hydrological compartments and flow paths. *Aquatic Geochemistry* 11, 57-88.
- Jacobsen, S. B., Wasserburg, G., 1980. Sm-Nd isotopic evolution of chondrites. *Earth Planet. Sci. Lett.* 50(1), 139-155.
- Kempton, P. D., Downes, H., Neymark, L. A., Wartho, J. A., Zartman, R. E., Sharkov, E. V., 2001. Garnet granulite xenoliths from the northern Baltic Shield – the underplated lower crust of a palaeoproterozoic large igneous province? *J. Petrol.* 42(4), 731-763.
- Klyunin, S., Grokhovskaya, T., Zakharov, A., Solovjeva, T., 1994. Geology and platinum-bearing potential of the Olanga group of massifs, Northern Karelia (in Russian). *Geologiya i genesis mestorozhdenii platinovykh metallov*. Nauka, Moscow, 111-126.
- Koptev-Dvornikov, E. V., 2001. Distribution of cumulative mineral assemblages, major and trace elements over the vertical c of the Kivakka intrusion, Olanga group of intrusions, Northern Karelia. *Petrology* 9(1), 3-27.
- Kulikov, V., Kulikova, V., 1982. On the summary section of the early Precambrian of the Vetreny belt (in Russian). *Geology and Stratigraphy of Karelian Precambrian Rocks*. Petrozavodsk, Year Book Information, 21-26.
- Kulikov, V., 1999. Komatiitic Basalts of the Vetreny Belt (in Russian). *Selected Works of the Karelian Scientific Center of Russian Academy of Sciences*, 60-61.
- Kulikov, V., Kulikova, V., Bychkova, Y., Zudin, A., 2003. Sumian rifting volcanism of Paleoproterozoi in South-Eastern part of Karelian Kraton. *Proceedings of the II All-Russian symposium on volcanology and paleovolcanology “Vulkanizm i geodinamika”*. Ekaterinburg, 99-104.
- Kulikov, V., Bychkova, Y., Kulikova, V., Koptev-Dvornikov, E., Zudin, A., 2005. Role of deep-seated differentiation in formation of Paleoproterozoic Sinegorie lava plateau of komatiite basalts, southeastern Fennoscandia. *Petrology* 13(5), 469-488.
- Kulikova, V.V., Kulikov, V.S., 1981. New data on Archean peridotitic komatiites in East Karelia. *Dokl. Akad. Nauk SSSR*. 259(3), 693-697.
- Kump, L. R., Brantley, S. L., Arthur, M. A., 2000. Chemical weathering, atmospheric CO₂, and climate. *Annu. Rev. Earth Planet. Sci. Lett.* 28, 611-667.
- Land, M., Ingri, J., Öhlander, B., 1999a. Past and present weathering rates in northern Sweden. *Appl. Geochem.* 14, 761-774.
- Land, M., Öhlander, B., Ingri, J., Thunberg, J., 1999b. Solid speciation and fractionation of rare earth elements in a spodosol profile from northern Sweden as revealed by sequential extraction. *Chem. Geol.* 160, 121-138.
- Land, M., Ingri, J., Andersson, P. S., Öhlander, B., 2000. Ba/Sr, Ca/Sr and ⁸⁷Sr/⁸⁶Sr ratios in soil water and groundwater: implications for relative contributions to stream water discharge. *Appl. Geochem.* 15, 311-325.
- Land, M., Öhlander, B., 2000. Chemical weathering rates, erosion rates and mobility of major and trace elements in a boreal granitic till. *Aquat. Geochem.* 6, 435-460.
- Land, M., Thunberg, J., Öhlander, B., 2002. Trace metal occurrence in a mineralised and a non-mineralised spodosol in northern Sweden. *J. Geochem. Explor.* 75, 71-91.

- Lavrov, M., 1979. Ultramafic and layered peridotite-gabbro-norite intrusions in Precambrian in Northern Karelia. Nauka, Leningrad, 135 p.
- Lesovaya, S., Goryachkin, S., Pogochev, E., Polekhovskii, Y., Zavarzin, A., Zavarzina, A., 2008. Soils on hard rocks in the Northwest of Russia: Chemical and mineralogical properties, genesis, and classification problems. *Eurasian Soil Science* 41(4), 363-376.
- Lesovaya, S., Goryachkin Yu, S.V., Polekhovskii, S., 2012. Soil formation and weathering on ultramafic rocks in the mountainous tundra of the Rai-Iz massif, Polar Urals. *Eurasian Soil Science* Volume 45, Issue 1, pp 33–44.
- Li, C., Yang, S., 2010. Is chemical index of alteration (CIA) a reliable proxy for chemical weathering in global drainage basin? *Am. J. Sci.* 310, 111-127.
- Lobach-Zhuchenko, S., Levchenkov, O., Cherulaev, V., Krylov, I., 1986. Geological evolution of the Karelian granite-greenstone terrain. *Precambrian Res.* 33(1-3), 45-65.
- Lobach-Zhuchenko, S., Chekulayev, V., Sergeev, S., Levchenkov, O., Krylov, I., 1993. Archaean rocks from southeastern Karelia (Karelian granite greenstone terrain). *Precambrian Res.* 62(4), 375-397.
- Lobach-Zhuchenko, S., Arestova, N., Chekulayev, V., Levsky, L., Bogomolov, E., Krylov, I., 1998. Geochemistry and petrology of 2.40-2.45 Ga magmatic rocks in the north-western Belomorian Belt, Fennoscandian Shield, Russia. *Precambrian Res.* 92, 223-250.
- Louvat, P., Allègre, C. J., 1997. Present denudation rates on the island of Réunion determined by river geochemistry: Basalt weathering and mass budget between chemical and mechanical erosions. *Geochim. Cosmochim. Acta* 61(17), 3645-3669.
- Louvat, P., Allègre, C. J., 1998. Riverine erosion rates on Sao Miguel volcanic island, Azores archipelago. *Chem. Geol.* 148(3-4), 177-200.
- Lozovik, P., Potapova, I., 2006. Input of chemical substances with atmospheric precipitation onto the territory of Karelia. *Water Resour.* 33(1), 104-111.
- Lundström, U., 1993. The role of organic acids in soil solution chemistry in a podzolized soil. *J. Soil Sci.* 44, 121-133.
- Lundström, U. S., van Breemen, N., Bain, D., 2000a. The podzolization process. A review. *Geoderma* 94, 91-107.
- Lundström, U. S., van Breemen, N., Bain, D. et al., 2000b. Advances in understanding the podzolization process resulting from a multidisciplinary study of three coniferous forest soils in the Nordic Countries. *Geoderma* 94(2-4), 335-353.
- Maher, K., 2011. The role of fluid residence time and topographic scales in determining chemical fluxes from landscapes. *Earth Planet. Sci. Lett.*, 312, 48-58.
- Maher, K., Chamberlain, C.P., 2014. Hydrologic regulation of chemical weathering and the geologic. *Science*, 343, 1502-1504.
- Maksimova, M., 1967. Inorganic and organic composition of major ions in rivers of Karelian coast of the White Sea (in Russian). *Gidrobiologicheskie issledovaniya na Karelskom poberezhie Belogo morya*. Nauka, Leningrad, 9-20.
- Melkerud, P., Bain, D., Jongmans, A., Tarvainen, T., 2000. Chemical, mineralogical and morphological characterization of three podzols developed on glacial deposits in Northern Europe. *Geoderma* 94, 125-148.
- Meunier, A., Caner, L., Hubert, F., El Alabani, A., Prêt D., 2013. The weathering intensity scale (WIS) : an alternative approach of the chemical index of alteration. *American Journal of Science*, Vol.313, 113–143.
- Millot, R., Gaillardet, J., Dupré, B., Allègre, C.J., 2002. The global control of silicate weathering rates and the coupling with physical erosion: new insights from rivers of the Canadian Shield. *Earth Planet. Sci. Lett.* 196, 83–98.
- Millot, R., Gaillardet, J., Dupré, B., Allègre, C. J., 2003. Northern latitude chemical

1094 weathering rates: Clues from the Mackenzie River basin, Canada. *Geochim.*
1095 *Cosmochim. Acta* 67(7), 1305-1329.

1096 Mokma, D., Yli-Halla, M., Lindqvist, K., 2004. Podzol formation in sandy soils of Finland.
1097 *Geoderma* 120, 259-272.

1098 Muir, A., 1961. The podzol and podzolic soils. *Advances in Agronomy* 13, 1-56.

1099 Murashkina, M., Southard, R., Pettygrove, G., 2007. Silt and fine sand fractions dominate K
1100 fixation in soils derived from granitic alluvium of the San Joaquin Valley, California.
1101 *Geoderma* 141, 283-293.

1102 Nesbitt, H. W., Young, G. M., 1982. Early Proterozoic climates and plate motions inferred
1103 from major element chemistry of lutites. *Nature* 299, 715-717.

1104 Öhlander, B., Ingri, J., Ponter, C., 1991. Geochemistry of till weathering in the Kalix River
1105 Watershed, northern Sweden. Reports in forest ecology and forest soils, Swedish
1106 University of Agricultural Sciences. In: Chemical weathering under field conditions
1107 (ed. K. Rosén) 63, 1-18.

1108 Öhlander, B., Land, M., Ingri, J., Widerlund, A., 1996. Mobility of rare earth elements during
1109 weathering of till in northern Sweden. *Appl. Geochem.* 11, 93-99.

1110 Öhlander, B., Thunberg, J., Land, M., Hoglund, L. O., Quishang, H., 2003. Redistribution of
1111 trace metals in a mineralized spodosol due to weathering, Liikavaara, northern
1112 Sweden. *Appl. Geochem.* 18, 883-899.

1113 Oliva, P., Viers, J., Dupré, B., Fortune, J. P., Martin, F., Braun, J.-J., Nahon, D., Robain, H.,
1114 1999. The effect of organic matter on chemical weathering: Study of a small tropical
1115 watershed: Nsimi-Zoétéélé site, Cameroon. *Geochim. Cosmochim. Acta* 63(23/24),
1116 4013-4035.

1117 Oliva, P., Dupré, B., Martin, F., Viers, J., 2004. The role of trace minerals in chemical
1118 weathering in a high-elevation granitic watershed (Estibère, France): Chemical and
1119 mineralogical evidence. *Geochim. Cosmochim. Acta* 68(10), 2223-2244.

1120 Olsson, M. T., Melkerud, P., 2000. Weathering in three podzolized pedons on glacial deposits
1121 in northern Sweden and central Finland. *Geoderma* 94, 149-161.

1122 Opfergelt, S., Burton, K.W., Georg, R.B., West, A.J., Guicharnaud, R.A., Sigfusson, B.,
1123 Siebert, C., Gislason, S.R., Halliday, A.N., 2014. Magnesium retention on the soil
1124 exchange complex controlling Mg isotope variations in soils, soil solutions and
1125 vegetation in volcanic soils, Iceland. *Geochim. Cosmochim. Acta* 125, 110-130.

1126 Parry, S.A., Hodson, M.E., Kemp, S.J., Oelkers, E.H., 2015. The surface area and reactivity
1127 of granitic soils: I. Dissolution rates of primary minerals as a function of depth and age
1128 deduced from field observations. *Geoderma* 237-238, 21-35.

1129 Peuraniemi, V., Aario, R., Pulkkinen, P., 1997. Mineralogy and geochemistry of the clay
1130 fraction of till in northern Finland. *Sedimentary Geology* 111, 313-327.

1131 Pokrovsky, O.S., Schott, J., 2002. Iron colloids/organic matter associated transport of major
1132 and trace elements in small boreal rivers and their estuaries (NW Russia). *Chem. Geol.*
1133 190, 141-179.

1134 Pokrovsky, O.S., Schott, J., Kudryavtsev, D. I., Dupré, B., 2005. Basalt weathering in Central
1135 Siberia under permafrost conditions. *Geochim. Cosmochim. Acta* 69(24), 5659-5680.

1136 Pokrovsky, O. S., Schott, J., Dupré, B., 2006a. Trace element fractionation and transport in
1137 boreal rivers and soil porewaters of permafrost-dominated basaltic terrain in Central
1138 Siberia. *Geochim. Cosmochim. Acta* 70, 3239-3260.

1139 Pokrovsky, O.S., Schott, J., Dupré, B., 2006b. Basalt weathering and trace elements migration
1140 in the boreal Arctic zone. *J. Geochem. Explor.* 88, 304-307.

1141 Ponomareva, V., 1964. Theory of podzol-formation process (in Russian). M.-L.: Nauka, p.
1142 380.

1143 Puchtel, I., Hofmann, A., Mezger, K., Shchipansky, A., Kulikov, V., Kulikova, V., 1996.

- 1144 Petrology of a 2.41 Ga remarkably fresh komatiitic basalt lava lake in Lion Hills,
1145 central Vetreny Belt, Baltic Shield. *Contrib. Mineral. Petrol.* 124(3-4), 273-290.
- 1146 Puchtel, I. S., Haase, K. M., Hofmann, A. W., Chauvel, C., Kulikov, V. S., Garbe-Schonberg,
1147 C., Nemchin, A. A., 1997. Petrology and geochemistry of crustally contaminated
1148 komatiitic basalts from the Vetreny Belt, southeastern Baltic Shield: Evidence for an
1149 early Proterozoic mantle plume beneath rifted Archean continental lithosphere.
1150 *Geochim. Cosmochim. Acta* 61(6), 1205-1222.
- 1151 Raymon, P.A., 2017. Temperature versus hydrological controls of chemical weathering fluxes
1152 from United States forests. *Chem. Geol.* 458, 1-13.
- 1153 Reimann, C., Melezhik, V., 2001. Metallogenic provinces, geochemical provinces and
1154 regional geology - what causes large-scale patterns in low density geochemical maps
1155 of the C-horizon of podzols in Arctic Europe? *Appl. Geochem.* 16(7-8), 963-983.
- 1156 Remaury, M., Oliva, P., Guillet, B., Martin, F., Toutain, F., Dagnac, J., Belet, J., Dupré, B.,
1157 Gauquelin, T., 2002. Nature and genesis of spodic horizons characterized by inverted
1158 color and organic content in a subalpine podzolic soil (Pyrenees Mountains, France).
1159 *Bulletin de la Société Géologique de France* 172(1), 77-86.
- 1160 Revyako, N., Bychkova, Y., Kostitsyn, Y., 2007. Isotope evidence of the interaction of basic
1161 melt with crust rocks on the example of Kivakka layered intrusion (Karelia) (in
1162 Russian). *Proceedings of International conference "Ultrabasic-basic complexes of fold
1163 regions"*. Irkutsk, 487-490.
- 1164 Riebe, C. S., Kirchner, J. W., Granger, D. E., Finkel, R. C., 2001 Strong tectonic and weak
1165 climatic control of long-term chemical weathering rates. *Geology* 29, 511-514.
- 1166 Riebe, C. S., Kirchner, J. W., Finkel, R. C., 2004. Erosional and climatic effects on long-term
1167 chemical weathering rates in granitic landscapes spanning diverse climate regimes.
1168 *Earth Planet. Sci. Letters* 224, 547-562.
- 1169 Righi, D., Chauvel, A., 1987. Podzols and Podzolization. *Assoc. Franc. Etude Sol. INRA,*
1170 *Plaisir et Paris, Paris.*
- 1171 Ryabchikov, I., Suddaby, P., Giris, A., Kulikov, V., Kulikova, V., Bogatkov, O., 1988.
1172 Trace-element geochemistry of Archaean and Proterozoic rocks from eastern Karelia,
1173 USSR. *Lithos* 21, 183-194.
- 1174 Salminen, R., Gregorauskiene, V., Tarvainen, T., 2008. The normative mineralogy of 10 soil
1175 profiles in Fennoscandia and north-western Russia. *Appl. Geochem.* 23(12), 3651-
1176 3665.
- 1177 Sarala, P., 2005. Till geochemistry in the ribbed moraine area of Peräpohjola, Finland. *Appl.*
1178 *Geochem.* 20, 1714-1736.
- 1179 Sawhney, B.L., 1989. Minerals in soil environments. *Soil Science Society of America,*
1180 *chapter 16: Interstratification in layer silicates, 789-828.*
- 1181 Schopka, H., Derry, L., Arcilla, C., 2011. Chemical weathering, river geochemistry and
1182 atmospheric carbon fluxes from volcanic and ultramafic regions on Luzon Island, the
1183 Philippines. *Geochim. Cosmochim. Acta* 75, 978-1002. Schopka, H., Derry, L., 2012.
1184 Chemical weathering fluxes from volcanic islands and the importance of groundwater:
1185 The Hawaiian example. *Earth and Planetary Science Letters* 339-340, 67-78.
- 1186 Schroeder, P.A., Melear, N.D., West, L.T., Hamilton, D.A., 2000. Meta-gabbro weathering in
1187 the Georgia Piedmont, USA: implications for global silicate weathering rates. *Chem.*
1188 *Geol.* 163, 235-245.
- 1189 Schweda, P., Araujo, P. D. R., Sjöberg, L., 1991. Soil chemistry, clay mineralogy and
1190 noncrystalline phases in soil profiles from southern Sweden and Gårdsjön.. In: Rosén,
1191 K. (Ed.), *Chemical weathering under field conditions. Reports in Forest Ecology and
1192 Forest Soils.* Swedish University of Agricultural Sciences 63, 49-62.
- 1193 Semenov, V., Koptev-Dvornikov, E., Berkovskii, A., Kireev, B., Pchelintseva, N., Vasil'eva,

- M., 1995. Layered troctolite-gabbro-norite Tsipinga intrusion, Northern Karelia: Geologic structure and petrology. *Petrology* 3(6), 588-610.
- Shmygalev, V., 1968. Mafic and ultramafic intrusions of the Olanga group. Proterozoic volcanic and ultramafic complexes of Karelia 1, 209-219.
- Simonsson, M., Bergholm, J., Olsson, B.A., von Brömssen, C., Öborn, I., 2015. Estimating weathering rates using base cation budgets in a Norway spruce stand on podzolised soil: Analysis of fluxes and uncertainties. *Forest Ecol. Management*, 340, 135-152.
- Starr, M., Lindroos, A., Ukonmaanaho, L., Tarvainen, T., Tanskanen, H., 2003. Weathering release of heavy metals from soil in comparison to deposition, litterfall and leaching fluxes in a remote, boreal coniferous forest. *Appl. Geochem.* 18, 607-613.
- State Geological Map of Russian Federation, 2001. In: Bogdanov, Yu.B. (Ed.), *Explication Note*. Ministry of Natural Resources, St-Petersbourg, VSEGEI. Sheet Q-(35)-37.
- Sun, X., Mörtz, C.-M., Humbord, C., Gustafsson, B., 2017. Temporal and spatial variations of rock weathering and CO₂ consumption in the Baltic Sea catchment. *Chem. Geol.* 466, 57-69.
- Stroeven, A.P., Hättestrand, C., Kleman, J., Heyman, J., Fabel, D., Fredin, O., Goodfellow, B.W., Harbor, J.M., Jansen, J.D., Olsen, L., 2016. Deglaciation of Fennoscandia. *Quaternary Sci. Rev.* 147, 91-121.
- Taylor, S., McLennan, S., 1985. *The continental crust: its composition and evolution*. Blackwell Scientific Publications, Oxford, p. 312.
- Thiede, J., Bauch, H. A., Hjort, C., Mangerud, J., 2001. The late Quaternary stratigraphy and environments of northern Eurasia and the adjacent Arctic seas - new contributions from QUEEN. *Global and Planetary Change* 31(1-4), vii-x.
- Thorn, C.E., Dixon, J.C., Darmody, R.G., Allen, C.E., 2006. A 10-year record of the weathering rates of surficial pebbles in Kärkevagge, Swedish Lapland. *Catena* 65, 272-278.
- Tyler, G., 2004. Vertical distribution of major, minor, and rare elements in a Haplic Podzol. *Geoderma* 119, 277-290.
- Vasiliev, M.V., 2006. Specific features of Vetreny Belt paleorift intrusive systems (in Russian). M.Sc. thesis, Faculty of Geology, Moscow State University.
- Vasyukova, E., Pokrovsky, O.S., Viers, J., Oliva, P., Dupré, B., Martin, F., Candaudap, F., 2010. Trace elements in organic- and iron-rich surficial fluids of boreal zone: Assessing colloidal forms via dialysis and ultrafiltration. *Geochim. Cosmochim. Acta* 74, 449-468.
- Viers, J., Dupré, B., Braun, J., Deberdt, S., Angeletti, B., Ngoupayou, J. N., Michard, A., 2000. Major and trace element abundances, and strontium isotopes in the Nyong basin rivers (Cameroon): constraints on chemical weathering processes and elements transport mechanisms in humid tropical environments. *Chem. Geol.* 169, 211-241.
- Wymore, A.S., Brereton, R.L., Ibarra, D.E., Maher, K., McDowell, W.H., 2017. Critical zone structure controls concentration-discharge relationships and solute generation in forested tropical montane watersheds. *Water Resources Res.*, 53(7), 6279-6295.
- World reference base for soil resources (IUSS Working Group WRB, FAO), 2006.
- Zakharova, E., Pokrovsky, O. S., Dupré, B., Gaillardet, J., Efimova, L., 2007. Chemical weathering of silicate rocks in Karelia region and Kola peninsula, NW Russia: Assessing the effect of rock composition, wetlands and vegetation. *Chem. Geol.* 242, 255-277.
- Zilliacus, H., 1989. Genesis of De Geer moraines in Finland. *Sediment. Geol.* 62(2-4), 309-317.

Table 1. Soils and surface waters studied and their bedrock composition. Sample series from Vetreny Belt paleorift and Kivakka intrusion are defined as "V" and "K", respectively. Samples marked with "w" correspond to surface waters and with "ss" - to soil solutions.

Sample no.	Description	Bedrock composition
<u>Soils</u>		
V-4	Podzol	Komatiitic basalts, glacial deposits
V-7	Podzol	Komatiitic basalts, glacial deposits
V-9	Regosol	Gneisses, glacial deposits
V-15	Regosol	Peridotites
V-16	Podzol	Gneisses, glacial deposits
K-7	Podzol	Gneisses, glacial deposits
K-8	Podzol	Gneisses, glacial deposits
K-14	Podzol	Olivinite
K-29	Regosol	Gneisses, glacial deposits
K-37	Podzol	Gabbro-norites
<u>Waters</u>		
V-3-w	Surface water	Basalt
V-9-w	r. Ruiga	Basalt
V-10-w	Surface water from basalt field	Basalt
V-11-w	Surface water from basalt field	Basalt
V-12-w	r. Ruiga, upstream biofilms	Basalt
V-13-w	r. Ruiga, highest upstream	Basalt
V-15-w	Creek over ultramafites	Ultramafites
V-18-w	r. Nukhcha	Basalt
K-7-w	r. Palajoki, tributary	Gneisses, glacial deposits
K-8-w	Subsurface flow (right bank of the r. Palajoki)	Gneisses, glacial deposits
K-10-w	Swamp (corresponds to K-43 and K-44)	Gabbro-norites
K-12-w	Spring from a swamp	Gneisses, glacial deposits
K-13-w	River over olivenites	Olivinite
K-17-w	Subsurface flow	Norites
K-30-w	r. Vartambina downstream	Gneisses, glacial deposits
K-31-w	r. Vartambina upstream, tributary	Gneisses, glacial deposits
K-32-w	Swamp	Gabbro-norites
K-33-w	Stream	Gabbro-norites
K-38-w	Swamp	Gabbro-norites
K-39-w	Swamp	Gabbro-norites
K-41-w	r. Molodilny (springing from swamp)	Gabbro-norites
K-43-w	Swamp	Gabbro-norites
K-44-w	Swamp	Gabbro-norites
K-45-w	r. Palajoki	Gneisses, glacial deposits
<u>Soil solutions</u>		
V-16-ss	Soil water	Peridotites, olivinites
K-5-ss	Soil solution	Gabbro-norites
K-35-ss	Soil solution	Norites

Table 2. Major, trace elements ($\mu\text{g L}^{-1}$) and dissolved organic carbon (DOC) concentrations, and strontium isotopic ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) measured in the dissolved phase (i. e. < 0.22 (0.45) μm) in river and swamp waters from Vetreny Belt (sampled on 12-23 July 2004) and Kivakka intrusion zone (sampled on 10-19 July 2006). “nm” stands for not measured; “<dl” – below detection limit; “TDS” – total dissolved solids; “RW” – river water; “SW” – surface water; “SWW” – mire water; “SS” – soil solution; γ – felsic substratum; β – basaltic substratum; G-n – gabbro-norite; N – norite; Ol – olivinite; P – peridotite.

Vetreny Belt	V-9-w	V-12-w	V-13-w	V-15-w	V-18-w	V-10-w	V-11-w	V-3-w	V-16-sw
0.22 μm	RW	RW	RW	RW	RW	SW	SW	SW	SS
$\mu\text{g/l}$	β	β	β	P	β	β	β	β	P
pH	5.92	5.9	6.5	5.07	7.05	5.18	5.18	5.46	7.11
t°C	20	27	27	25	23	29	29	23	24
DOC, mg/l	36.5	34.7	35.7	39.7	17.2	8.8	98.5	9.8	20.6
Na ⁺	2 335	2 532	2 215	1 687	4 430	1 800	2 045	1 365	1 508
K ⁺	514	469	407	106	224	517	304	305	651
Mg ²⁺	2 867	2 793	6 034	3 128	2 917	425	328	544	8 023
Ca ²⁺	1 838	1 811	1 689	837	2 943	1 296	922	1 112	516
H ₄ SiO ₄	4 900	5 070	4 030	4 020	2 210	3 970	4 540	2 930	5 980
Cl ⁻	1 270	nm	1 590	2 080	3 900	1 582	2 460	1 350	2 210
SO ₄ ²⁻	750	nm	531	531	800	900	810	1 540	1 590
NO ₃ ⁻	<dl	<dl	480	295	101	100	<dl	290	539
F ⁻	70	<dl	<dl	39	56	28	<dl	33	<dl
[Alk], mg/l	4.85	5.56	16.6	2.05	28	4.21	4.84	1.77	29.89
Al	nm	537	340	319	56	264	310	244	161
Fe	1 888	865	752	2 374	2 216	618	135	290	311
Rb	0.52	0.59	0.53	0.38	0.48	0.85	0.41	0.56	0.76
Sr	13.00	12.18	11.19	5.08	18.81	11.99	9.24	10.11	4.15
TDS, mg/l	16.4	14.1	18.1	15.4	19.9	11.5	8.6	10.0	21.5
$^{87}\text{Sr}/^{86}\text{Sr}$	0.723799 ± 20	nm	nm	0.722741 ± 20	0.721984 ± 12	nm	nm	0.715087 ± 17	0.723249 ± 33

Table 2, continued.

Kivakka intrusion	K-7-w	K-8-w	K-12-w	K-30-w	K-31-w	K-45-w	K-13-w	K-17-w	K-33-w
0.45 µm	RW	RW	SW	RW	RW	RW	RW	SW	RW
µg/l	γ	γ	γ	γ	γ	γ	Ol	N	G-n
pH	7.36	5.95	6.56	7.42	7.45	7.31	6.56	6.72	6.13
t°C	16	6	nm	nm	nm	nm	nm	nm	nm
DOC, mg/l	10.42	1.74	5.60	6.32	5.08	94.36	30.55	2.22	6.41
Na ⁺	1 667	1 379	2 161	2 732	1 714	1 652	1 378	2 044	1 164
K ⁺	502	315	64	386	907	370	374	72	38
Mg ²⁺	2 106	674	1 451	3 898	7 874	1 821	13 002	1 218	570
Ca ²⁺	9 745	2 047	4 891	10 596	17 435	7 219	1 901	7 385	2 328
H ₄ SiO ₄	3 210	3 990	3 760	4 880	3 290	2 390	7 310	4 560	3 200
Cl ⁻	568	576	295	393	495	526	453	534	400
SO ₄ ²⁻	1 498	3 650	2 300	351	688	1 922	432	3 576	736
NO ₃ ⁻	<dl	<dl	<dl	<dl	139	<dl	<dl	<dl	<dl
F ⁻	<dl	<dl	<dl	<dl	<dl	<dl	<dl	<dl	<dl
[Alk], mg/l	27.38	8.28	22.76	39.42	80.20	28.32	40.21	26.17	9.59
Al	26.34	32.30	51.74	7.48	9.76	32.97	191.38	20.07	125.24
Fe	2 589.87	5.59	116.64	115.31	246.79	2 124.46	391.96	3.33	270.26
Rb	1.23	0.99	0.17	0.78	1.79	1.06	1.53	0.20	0.15
Sr	50.89	9.94	12.55	17.20	15.91	36.96	14.26	14.79	8.50
TDS, mg/l	19.30	12.63	14.92	23.24	32.54	15.90	24.85	19.39	8.44
⁸⁷ Sr/ ⁸⁶ Sr	0.721067 ± 15	0.725299 ± 15	0.716615 ± 15	nm	nm	0.721102 ± 12	0.717867 ± 21	0.713467 ± 19	nm

Table 2, continued.

Kivakka intrusion	K-41-w	K-10-w	K-43-w	K-44-w	K-32-w	K-38-w	K-39-w	K-5-ss	K-35-ss
0.45 µm	RW	SWW	SWW	SWW	SWW	SWW	SWW	SS	SS
µg/l	G-n	γ	G-n	G-n	G-n	G-n	G-n	N	G-n
pH	7.17	4.94	5.85	5.41	4.56	4.65	5.03	4.94	nm
t°C	nm	24	16	21	nm	19	nm	6	nm
DOC, mg/l	4.96	29.46	nm	31.59	16.65	11.60	5.28	3.43	40.34
Na ⁺	1 871	1 031	1 094	1 068	1 399	845	743	569	1 102
K ⁺	89	58	32	50	190	249	133	77	178
Mg ²⁺	1 068	832	1 327	1 055	384	217	165	114	674
Ca ²⁺	3 166	2 065	3 707	2 382	909	644	674	520	1 305
H ₄ SiO ₄	3 700	1 930	2 780	2 250	2 470	490	760	2 520	4 540
Cl ⁻	374	725	726	841	1 252	1 180	742	217	1 414
SO ₄ ²⁻	1 610	494	255	235	332	220	599	1 853	1 868
NO ₃ ⁻	<dl	<dl	<dl	<dl	<dl	<dl	<dl	862	595
F ⁻	<dl	<dl	<dl	<dl	<dl	<dl	<dl	<dl	<dl
[Alk], mg/l	16.61	nm	8.06	2.67	2.20	2.76	2.72	1.77	nm
Al	42.69	453.75	302.11	386.37	163.85	179.22	224.63	274.24	440.35
Fe	36.68	3 876.17	10 507.70	4 778.12	164.02	180.11	237.39	913.91	41.37
Rb	0.17	0.10	0.13	0.08	0.51	0.45	0.24	0.29	0.65
Sr	11.56	12.93	16.71	14.19	4.09	4.02	5.31	3.65	10.44
TDS, mg/l	11.88	11.5	20.7	13.0	7.3	4.2	4.3	7.9	12.2
⁸⁷ Sr/ ⁸⁶ Sr	0.713984 ± 13	nm	0.721347 ± 46	nm	nm	nm	nm	nm	nm

Table 3. Mineralogical composition of studied soils. Number of “+” signs indicates different degree of presence of a mineral in soil, “Tr.” stands for “traces”. Empty cells correspond to the absence of a mineral in the soil sample.

Mineral composition	Quartz	Feldspar	Amphibole	Illite	Vermiculite	Chlorite	Hydrobiotite	Amorphous phases	Interlayered Mica/Vermiculite	Smectite	Talc
K-7-B	+	++	+	+	++	Tr.					
K-14-B1	Tr.			+	+++	+					
K-14-C			+	+	+++	+					Tr.
K-29-O/A	++	++	+	++		Tr.	++	+	+		
K-29-E	++	++	Tr.	++		Tr.	++	+			
K-37-A	++	++	++	++							
K-37-B1	++	++	+	+	++	+				+	
K-37-B2	++	+	+	+	+	+					
V-16-E	++	++	++	+				++			
V-16-B	++	++	+	+	+			+			
V-4-E	++	+	Tr.	Tr.		+				++	
V-7-B	++	+	+	+	+	++		+			
V-9-A	++	+	+					+			
V-15-O/A			+	+	++					++	

Table 4. Chemical Depletion Fraction (CDF), Chemical Depletion Fraction of individual element (CDFx), Chemical Index of Alteration (CIA), CIA_{soil}/CIA_{rock} ratios and poles (4Si, R^{2+} and M^{+}) calculations for the Weathering Intensity Scale (WIS) diagram. CDF and CDFx were calculated according to Riebe et al. (2004). CIA values were calculated following Nesbitt and Young (1982) considering that all CaO content are coming from silicate phases. WIS poles were established using the reference study of Meunier et al., 2014 by considering monocationic millimoles from oxide amounts : $4Si = \text{mMol Si}/4$; $R^{2+} = \text{mMol Mg}^{2+} + \text{mMol Mn}^{2+}$; $M^{+} = \text{mMol Na}^{+} + \text{mMol K}^{+} + 2\text{mMol Ca}^{2+}$. The R^{2+} component was calculated without considering Fe^{2+} content because only total Fe was measured during chemical analyses.

Calculated chemical depletion fraction of elements, Ti as invariant												SOIL WIS			
	type of rock	Chemical depletion	% Si	% Al	% Fe	% Ca	% Mg	% Na	% K	% Mn	CIA	CIAsoil/CIArock	% 4Si	% M+	% R2+
SAMPLE															
soil samples															
K-7 E	γ	51%	0,3	0,6	0,9	0,9	1,0	-0,1	-3,8	0,9	50	1,01	54,96	41,76	3,27
K-7 B	γ	52%	0,3	0,7	0,7	0,9	0,9	0,0	-3,0	0,9	50	1,01	52,57	40,68	6,74
K-8 E	γ	2%	-0,1	0,3	0,5	0,7	0,4	0,1	-0,3	0,8	50	1,00	56,13	39,22	4,65
K-8 B	γ	-72%	-0,6	-0,2	-0,6	0,3	-0,2	-0,3	-0,7	0,6	54	1,08	54,26	39,90	5,84
K-8 C	γ	-29%	-0,4	0,1	0,2	0,4	-0,2	-0,3	-0,6	0,6	48	0,98	52,28	41,45	6,26
K-14 B1	Ol	63%	0,6	0,6	0,6	0,7	0,7	0,6	0,6	0,6	46	1,17	14,87	6,25	78,88
K-14 B2	Ol	81%	0,7	0,2	1,0	0,8	1,0	-1,0	-1,5	1,0	48	1,21	50,93	37,13	11,94
K-14 C	Ol	32%	0,3	0,4	0,3	0,4	0,3	0,7	0,9	0,3	42	1,06	13,91	5,14	80,95
K-29 O/A	γ	-520%	-0,5	-0,3	0,2	-0,1	0,2	-0,9	0,5	0,6	45	0,91	46,39	50,59	3,01
K-29 C	γ	-48%	-0,6	-0,3	0,5	-0,1	0,6	-0,9	0,6	0,7	49	0,98	48,03	48,26	3,70
K-29 E	γ	-51%	-0,4	-0,1	0,4	-0,3	0,4	-0,5	0,2	0,1	49	0,99	50,86	47,47	1,66
K-37 O	G-n	6%	0,3	0,6	0,7	0,9	0,9	0,1	-3,2	0,9	49	1,24	53,02	38,82	8,16
K-37 A	G-n	40%	0,3	0,6	0,7	0,9	0,9	0,0	-3,7	0,9	50	1,26	51,80	40,10	8,10
K-37 B1	G-n	33%	0,1	0,6	0,7	0,9	0,9	-0,2	-4,0	0,8	49	1,24	51,34	39,78	8,88
K-37 B2	G-n	23%	0,0	0,4	0,6	0,8	0,8	-0,4	-4,4	0,8	51	1,27	47,38	43,45	9,17
K-37 C	G-n	6%	-0,2	0,3	0,7	0,8	0,8	-0,8	-6,0	0,8	52	1,31	51,66	41,16	7,18
V4 E	β	-65%	-1,7	-0,1	0,9	0,8	1,0	-1,3	-4,9	0,8	52	1,34	66,07	30,71	3,22
V7 E	β	-51%	-1,1	-0,3	0,8	0,7	0,9	-1,3	-5,3	0,8	52	1,35	55,26	37,69	7,05
V7 B	β	-50%	-1,1	-0,4	0,5	0,7	0,8	-1,4	-5,1	0,6	53	1,38	49,09	35,88	15,03
V9 O	γ	-1671%	0,3	0,4	-0,3	-1,0	-0,8	0,6	-0,5	-1,4	32	0,65	25,83	54,88	19,29
V9 A	γ	15%	0,3	0,6	0,1	0,1	-0,8	0,7	0,7	0,4	37	0,75	38,45	37,11	24,44
V16 E	γ	-102%	-1,4	-0,3	0,6	0,2	0,5	-0,8	-1,2	0,7	51	1,02	59,71	36,35	3,94
V16 B	γ	-191%	-2,4	-1,2	-0,2	-0,2	-0,3	-1,8	-2,2	0,2	51	1,03	54,80	37,84	7,36
V15 O/A	P	-123%	-0,8	0,1	-0,9	-0,6	-2,5	0,5	0,5	-2,6	28	0,73	15,67	23,64	60,69
Rock samples															
Goletz Basalt											39		22,44	42,57	35,00
Gabbro-norite											40		22,88	51,73	25,39
TTG											50		43,63	49,91	6,46
Olivenite											40		13,48	6,15	80,37

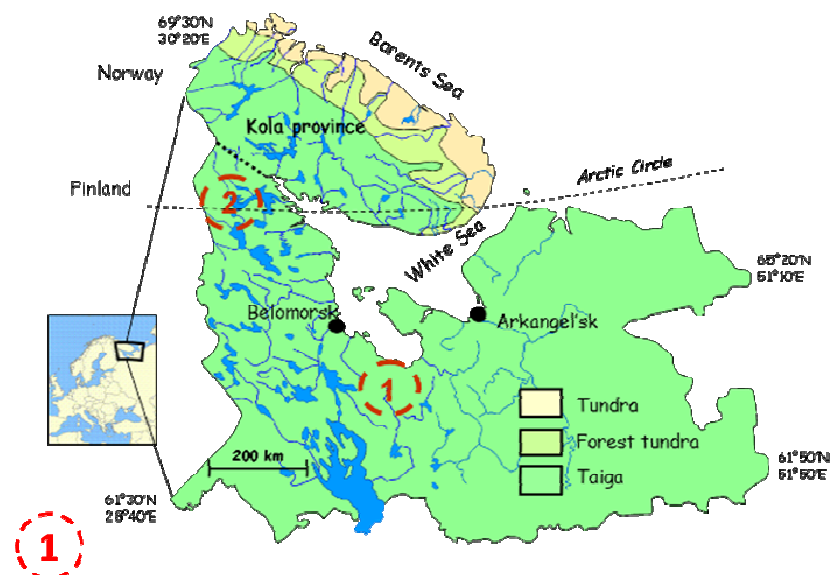
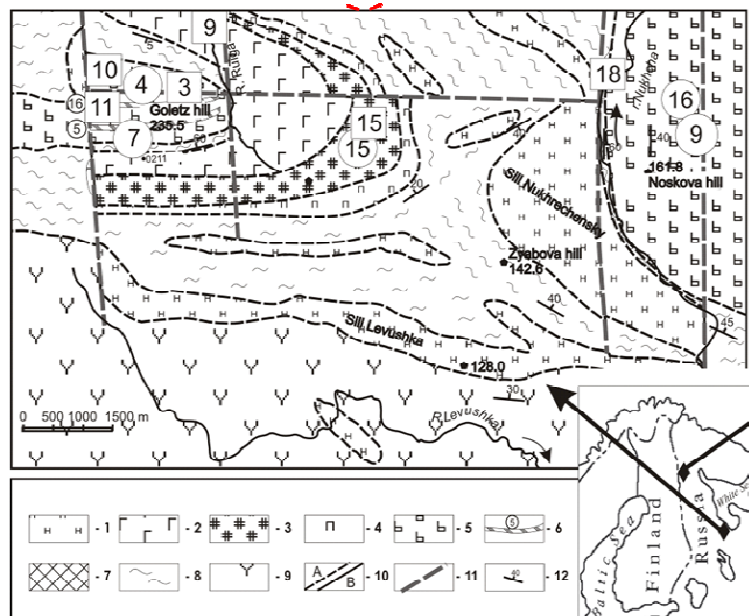


Fig. 1. Map of the studied areas Vetreny Belt paleorift (1) and Kivakka intrusion (2) showing soil (circles) and water (squares) sampling points and geological situation.

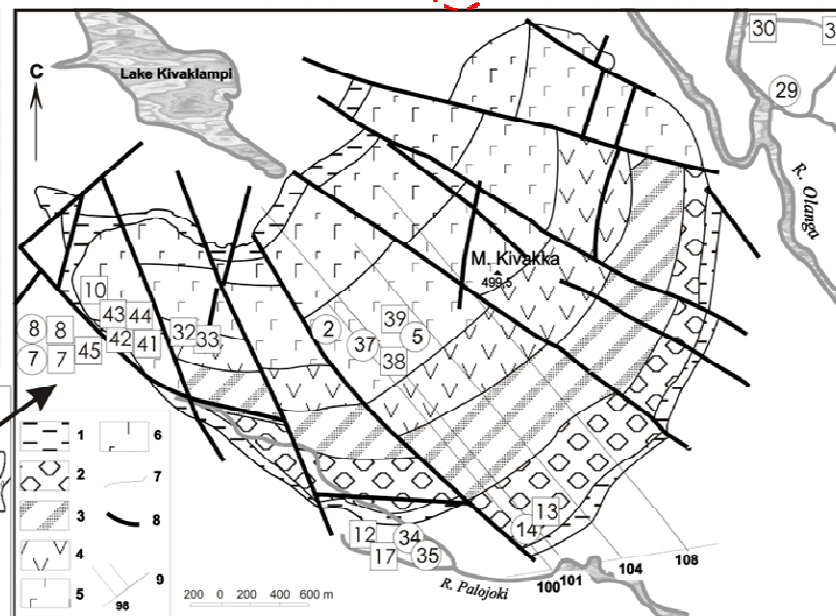


I. Schematic geological map of the Vetreny Belt (from Goletz hill to r. Nukhcha):

1 - nonsegmented mafit-ultramafit sills and dykes, 2 - gabbros, 3 - peridotites, 4 - pyroxenites, 5 - nonsegmented komatiitic basalts, 6 - differentiated covers 5 and 16 (in circles), 7 - probable supplying and deferent canals for prevolcanic camera Ruiga, 8 - Vileng suite sediments, 9 - Kirich suite vulcanites, 10 - geological borders (A - supposed, B - observed), 11 - faults, 12 - deposition elements.

Sample points and their numbers are marked with circles (soils) and squares (water).

Modified after Kulikov et al. (2008).



II. Schematic geological map of the Kivakka intrusion:

1 - Lower and Upper Contact Zones (LCZ and UCZ, respectively), 2 - Olivinite Zone (OZ), 3, 4 - Norite Zone (NZ), 3 - Subzone of Intercalating Bronzites and Norites (SIBN), 5 - Gabbro-Norite Zone (GNZ), 6 - Zone of Gabbro-Norites with Pigeonite (ZGNp), 7 - geological borders, 8 - faults, 9 - profiles of YUKE PGO Sevzapgeologiya.

Sample points and their numbers are marked with circles (soil) and squares (water).

Modified after Bychkova and Koptev-Dvornikov (2004).

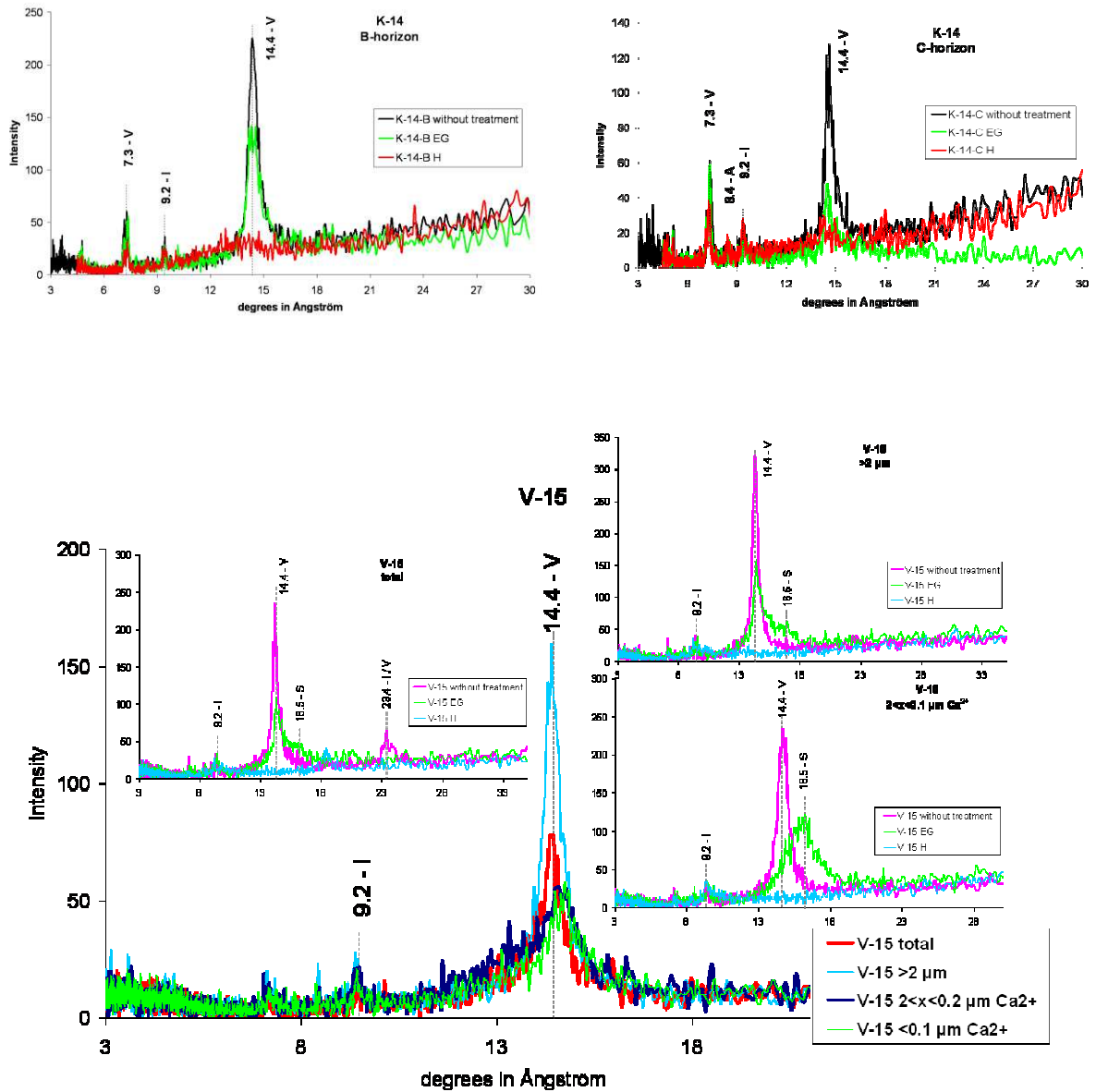


Fig. 2A. Representative X-ray diffractograms of soil profiles K-14 (upper panels) and V-15 (bottom panels). Minerals: I – illite, I/V – interstratified layers of illite and smectite, S – smectite, V – vermiculite. EG – ethylene-glycol saturation, H – heating, Ca^{2+} - calcium saturation.

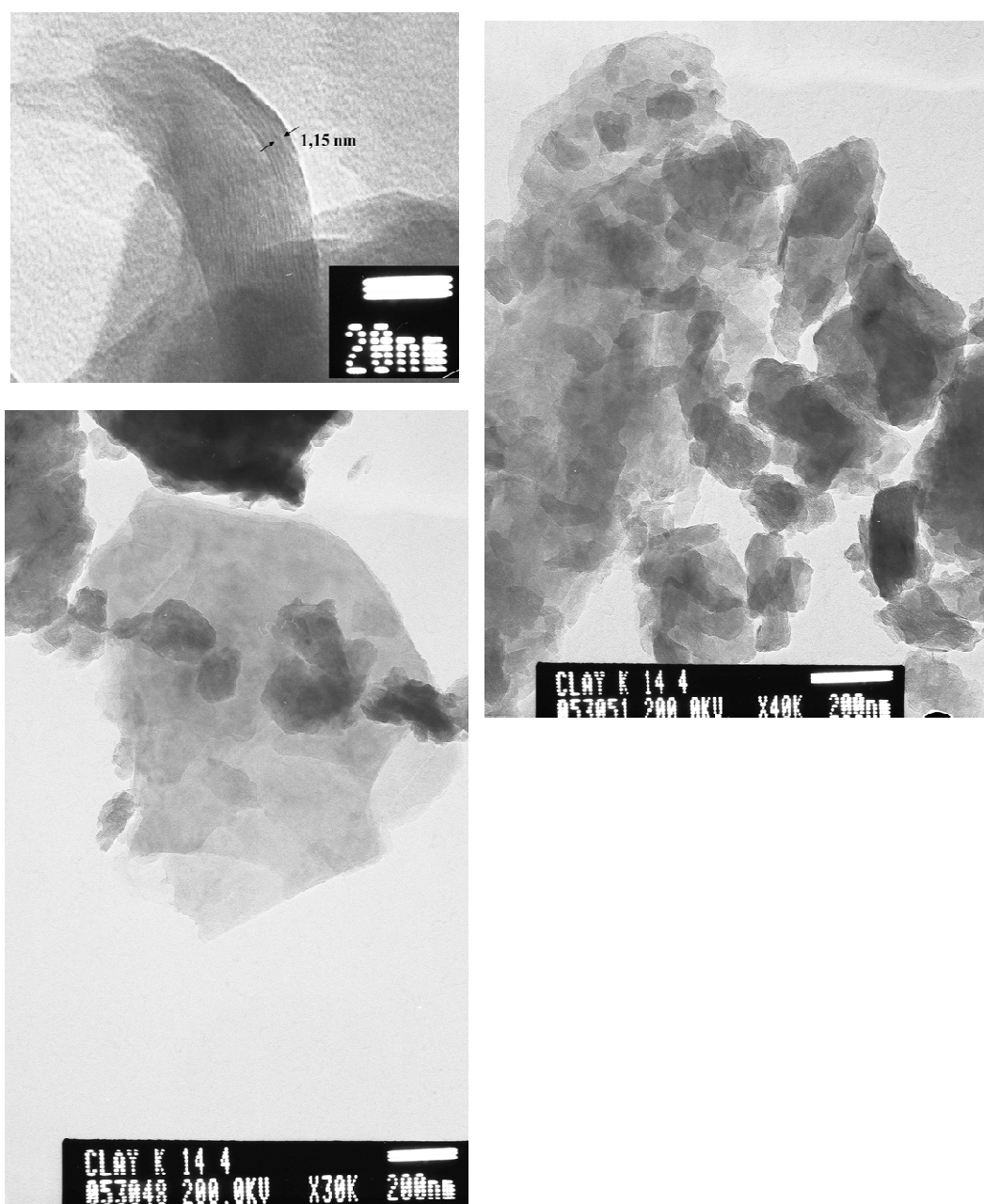


Fig. 2B. Transmission electron microscopy of clays in sample K-14.

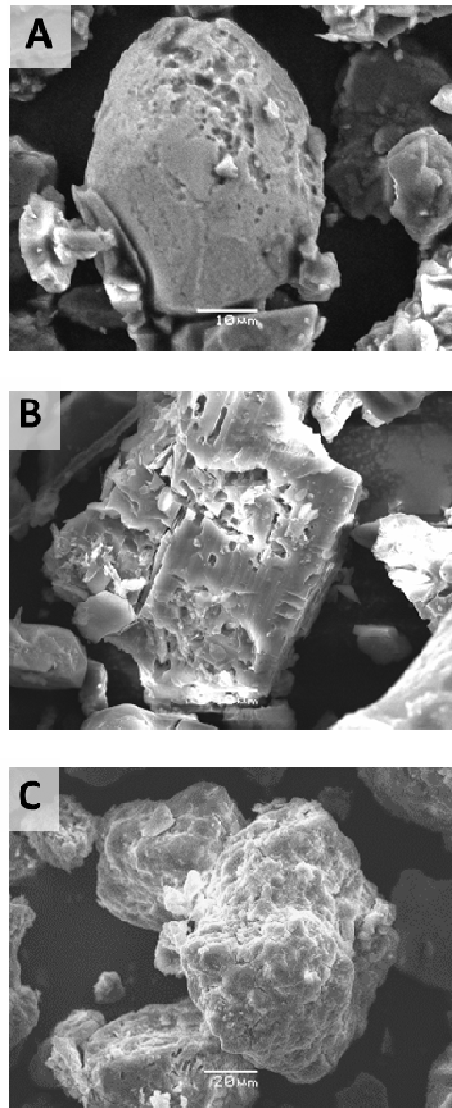


Fig. 3. SEM images of minerals found in soils illustrating neo-formed material and erosion on the surface of minerals: **A**, altered zircon in podzol V-16 over granite; **B**, altered feldspar in regosol K-29 over granite; **C**, quartz covered with aluminous coating in podzol K-37 over gabbro-norite.

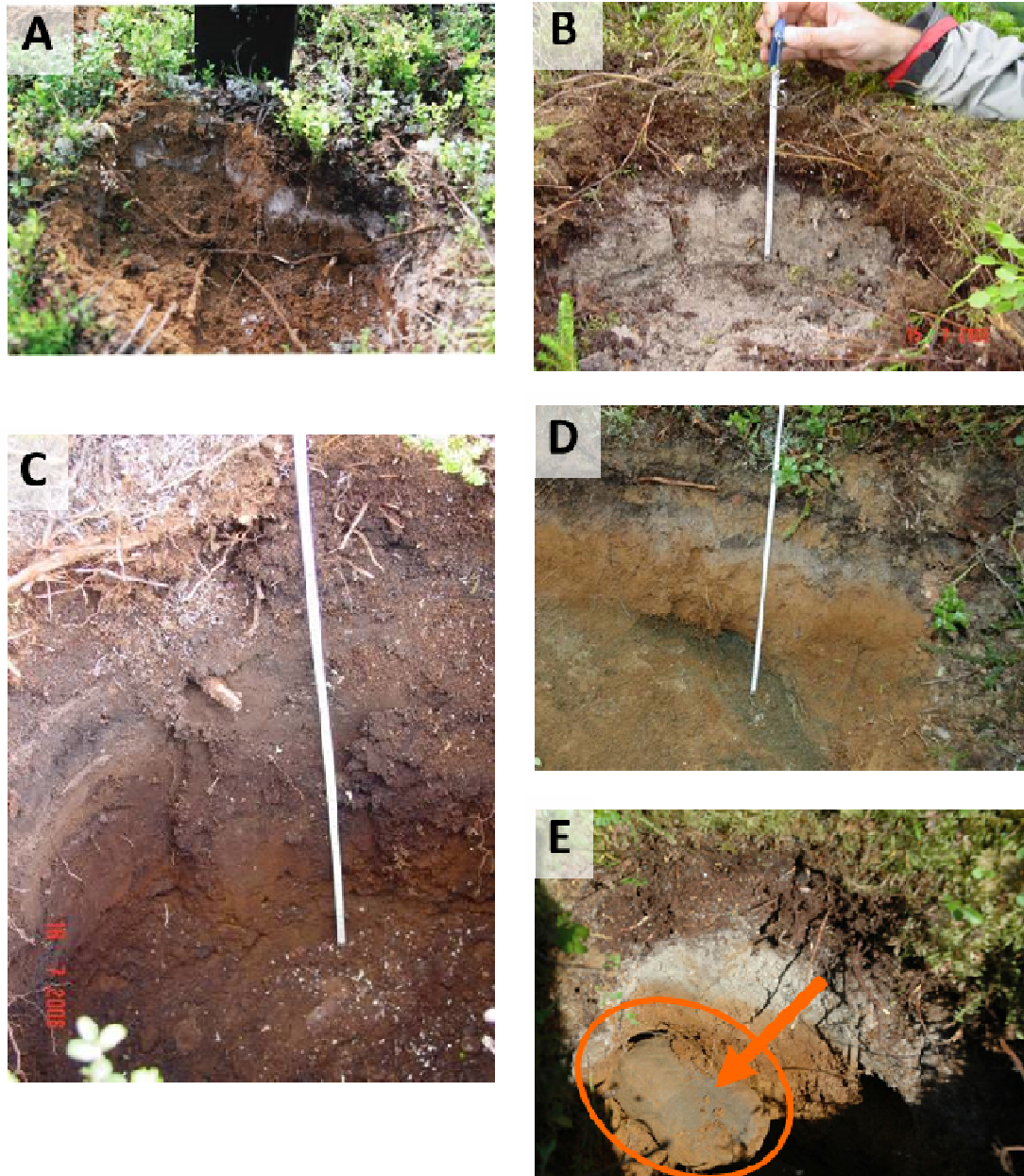


Fig. 4. Photos of podzol V-4 developed on komatiitic basalts from the Goletz hill of Vetreny Belt (A); the regosol K-29 under heather and bilberry bushes developed on gneiss from the Kivakka intrusion zone (B); the podzol K-37 developed on gabbro-norite rock of the Kivakka intrusion (C); the podzol K-14 developed on olivinite rock of the Kivakka intrusion (D) and podzol (K-7) developed on gneiss from the Kivakka intrusion zone (E). Full scale quaternary (Pleistocene) deposits can be observed in the deepest horizon confirming a strong moraine influence in this region.

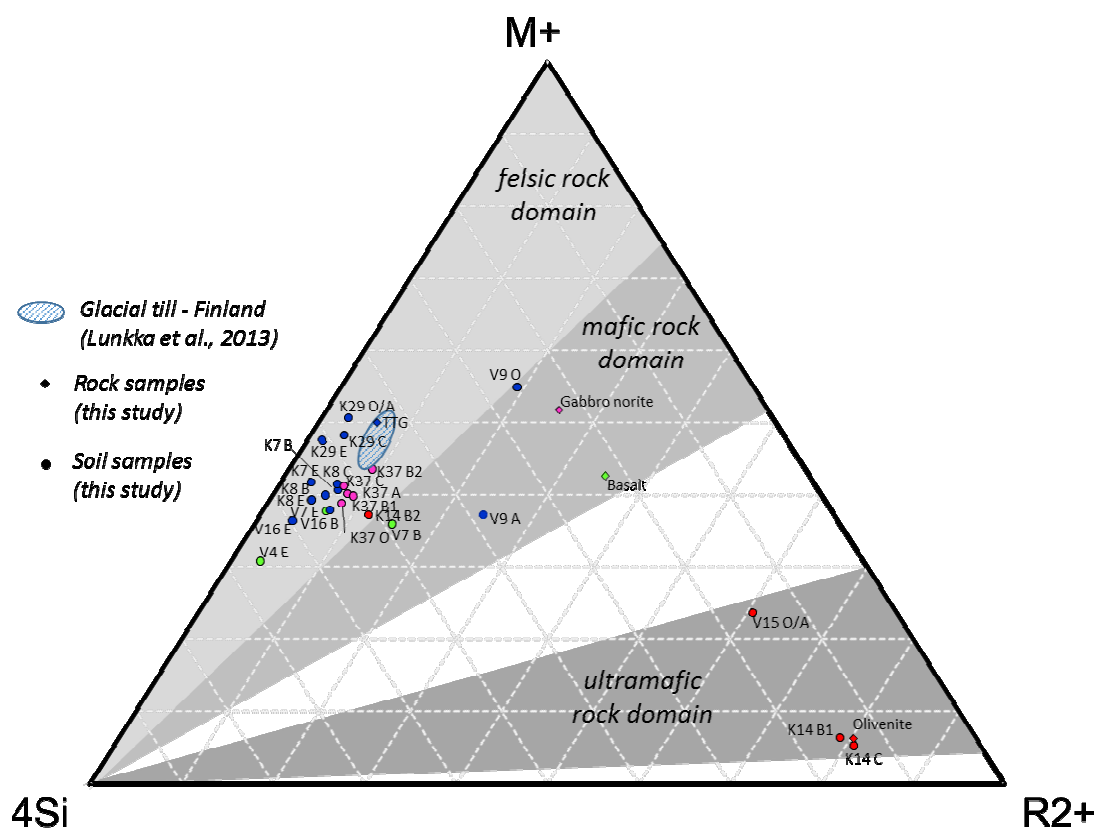


Fig. 5. WIS diagram including all the studied soil samples, Olivineite, Gabbro-norite, TTG rocks from Kivakka, Goltetz Basalt from Vetreny Belt and glacial till from Finland (Lunkka et al., 2013). See table 4 for calculations.

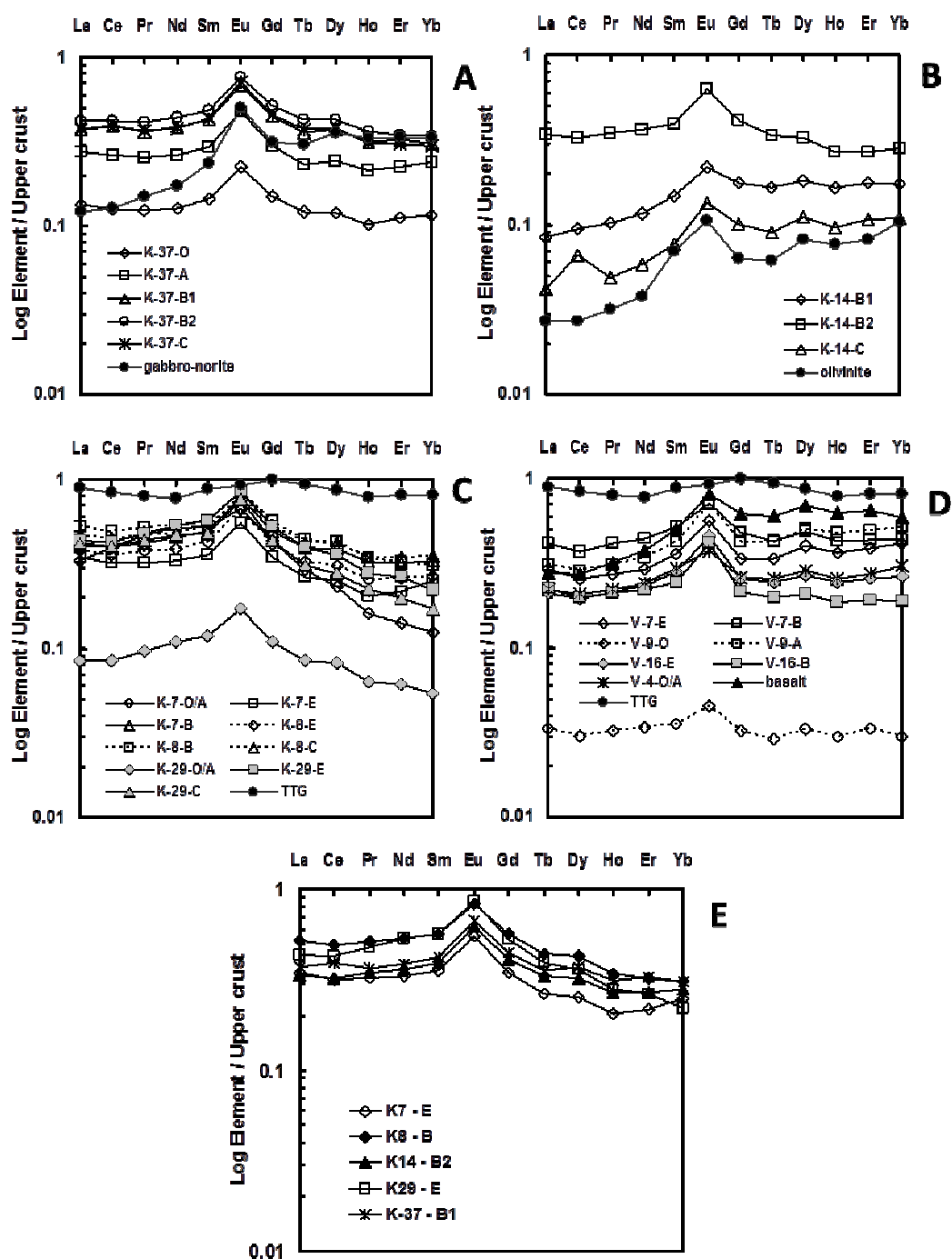


Fig. 6. Upper crust normalized REE patterns for soils from Kivakka intrusion (a, b, c), Vetreny Belt (d), and a mixed diagram on which E and B horizons of different soils are plotted (e). Average composition of the continental crust is taken from Taylor and MacLennan (1985); REE data on rocks of the Kivakka intrusion are from N. Krivolutskaya (unpublished data).

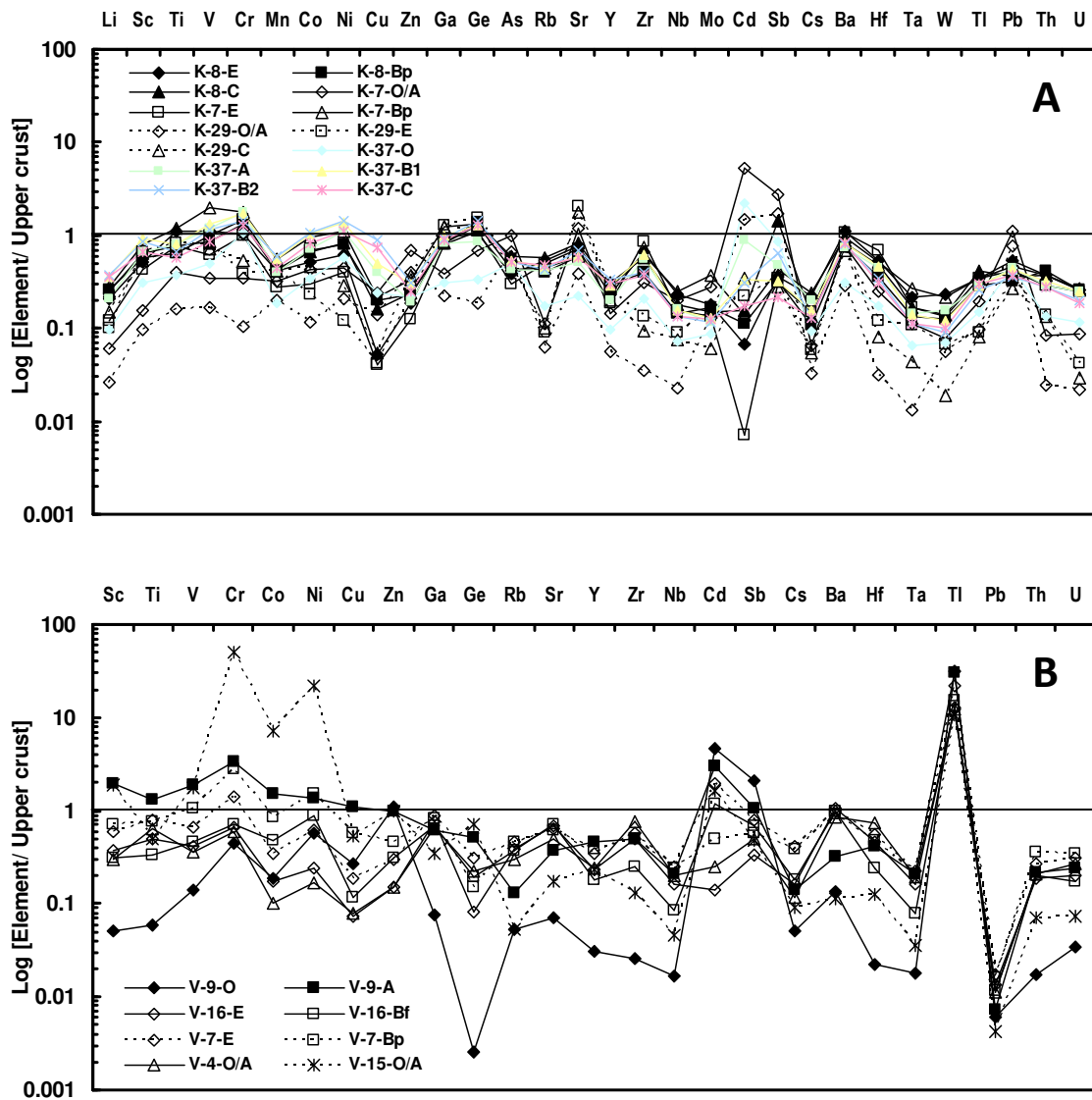


Fig. 7. Upper crust (Taylor and MacLennan, 1985) normalized extended elements patterns for soils developed on both felsic and mafic rocks from the Kivakka intrusion zone (A) and Vetreny Belt zone (B).

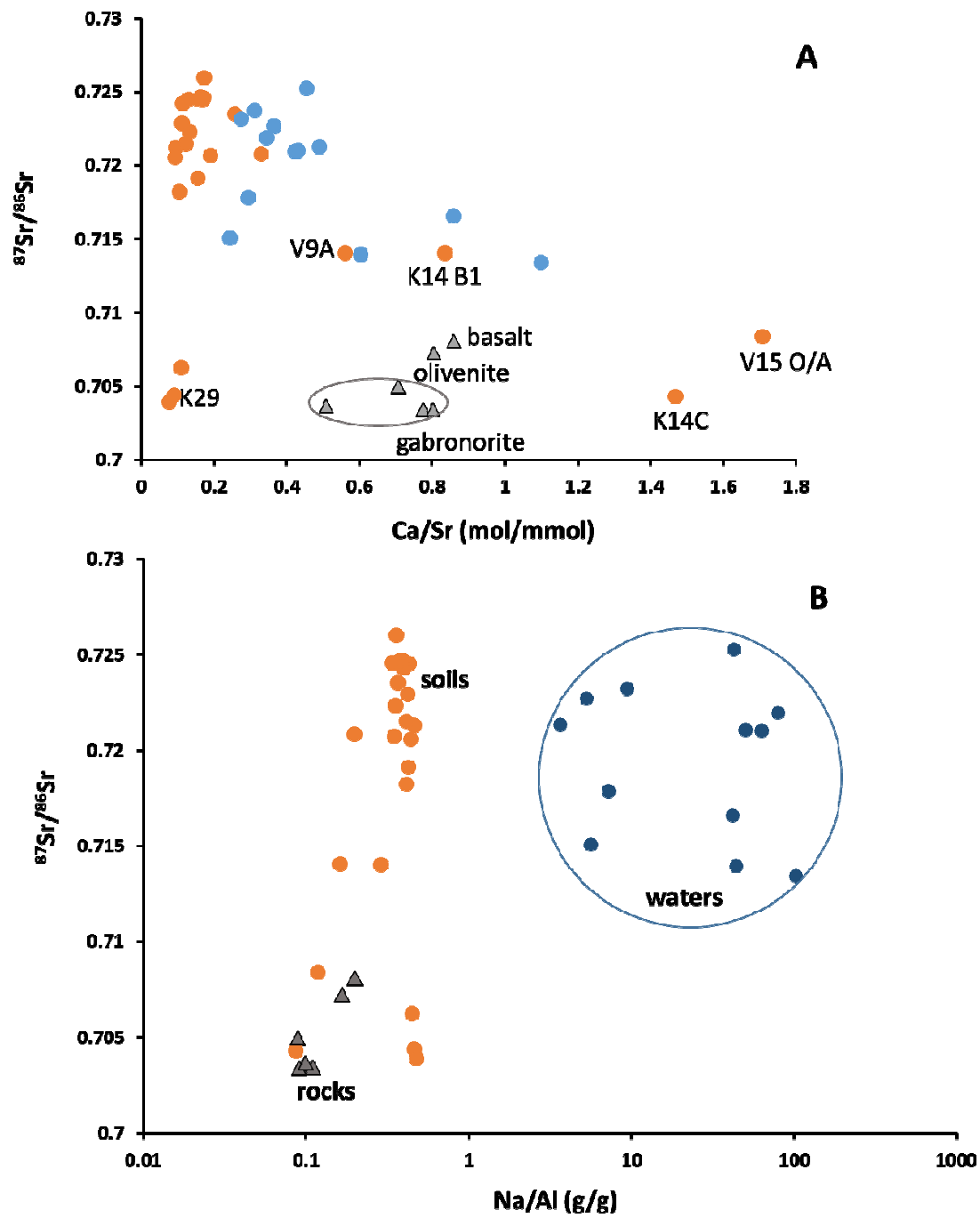


Fig. 8. Sr isotope ratio versus Ca/Sr ratio of soils and rocks (A) and Sr isotope ratio in soils, rocks and waters versus Na/Al ratio as indicator of weathering degree.

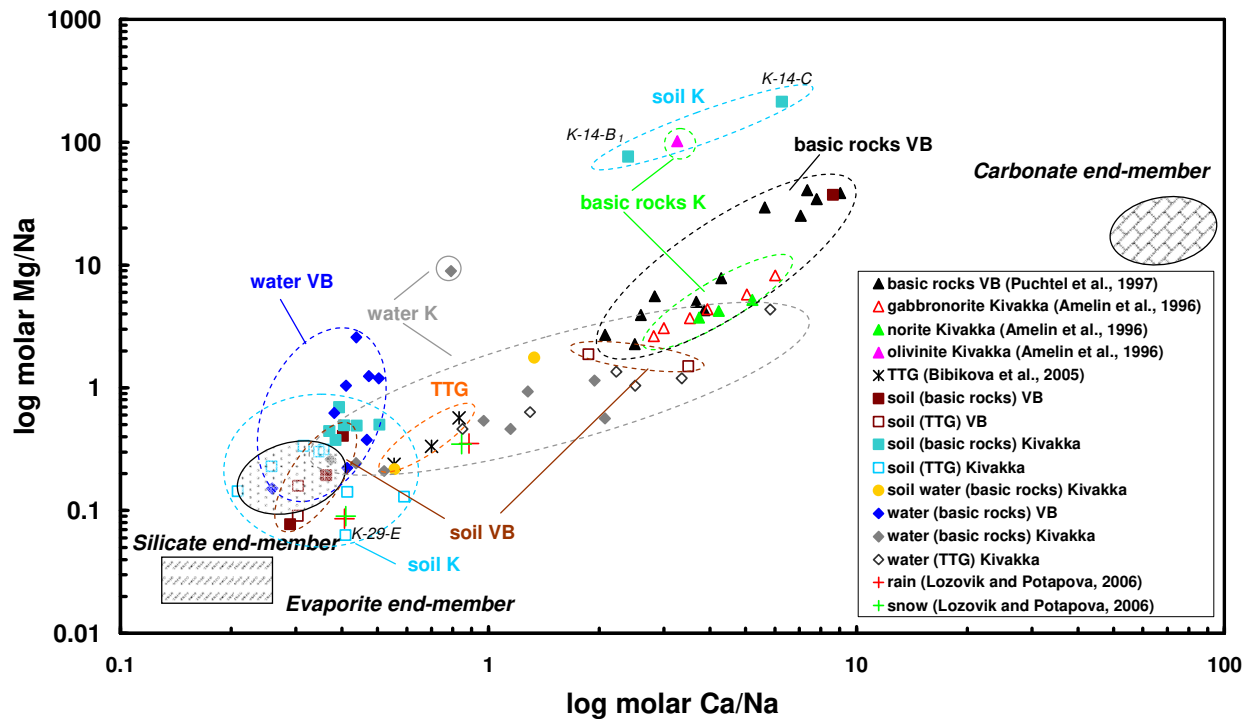


Fig. 9. Ca/Na molar ratios vs. Mg/Na molar ratios showing different materials (soils, rocks and waters) from Kivakka intrusion and Vetreny Belt (VB) zones. The carbonate, silicate, and evaporate end-members are taken from Gaillardet et al. (1999). Atmospheric signatures are calculated from the data reported by Lozovik and Potapova (2006). “VB” and “K” on the diagram stand for Vetreny Belt and Kivakka intrusion zones, respectively. Note that the scale of X and Y axes is different.

Chemical weathering of mafic rocks under granitic moraine in the subarctic

