Abiotic and Biotic Processes of Mineral Weathering in Tundra Soils on Ultramafic and Mafic Rocks of the Polar Urals, Russia

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Abstract The weathering of mafic and ultramafic rocks in soil environment was investigated in weakly developed soil profiles in order to determine the origin of phyllosilicate association in the soils formed in humid cold climate of the mountainous tundra of the Polar Urals. The objects of the study are represented by soils formed (i) on and underlain by the ultramafic rock and (ii) on the moraine composed of the mafic rock with an admixture of the ultramafic rock fragments. The minerals found in the clay fraction $\ll 1 \mu m$ of the profiles are the same, characterized by the presence of smectite (saponite), which is absent in both mafic and ultramafic rocks; serpentine and talc identified in ultramafic rock; and chlorite. Chlorite was found in both types of rocks. It was shown that the appearance of smectite (saponite) in the weakly developed soil is not related to pedogenesis. But these soil profiles illustrate the possibility of soil formation on "mature" fine earth formed from a high-sensitive ultramafic rock due to chemical weathering. In cold soil environment the more weatherable ultramafic material plays the more important role as a prerequisite for the weathering trends and soil formation than a mafic rock. The admixture of ultramafic materials mitigates the development of Entic Podzols which were earlier found in the Polar Urals on the pure mafic materials. So, the presence of ultramafic materials either predominating or even in admixture results in the "extreme lithological environment" for a pedogenesis and in the formation of weakly developed soils—Regosols and Leptosols.

Keywords Clay minerals \cdot Extreme environment for pedogenesis \cdot Metagabbro– amphibolite \cdot Serpentinous dunite \cdot Weakly developed soils

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1 Introduction

The challenge of the twenty-first century for both clay mineralogy and pedology includes the processes of weathering in extreme environment on the Earth that brings the bridge for understanding the relevant processes on the Mars and other planets. It concerns the desert environment as well as the polar one. The development of abiotic physical processes, including the disintegration initiated by freezing–thawing cycles is the most acceptable scenario of rock weathering in the cold environments. Nevertheless, the progress of chemical weathering limited by moisture availability in cold conditions has been shown (Hall et al. [2002\)](#page-12-0). The processes (physical and chemical) are coexisted in cold environments. That was confirmed by findings that disaggregation of a rock was stressed in the chemical weathering (Hoch et al. [1999](#page-12-0)) due to an increase of a surface area (Arnaud and Whiteside [1963](#page-12-0); Allen [2002\)](#page-12-0). Besides that, the microstructure properties of rocks influence the element release from them (Meunier et al. [2007\)](#page-13-0). Intensive chemical weathering affected by pedogenesis, which was led to the smectite (saponite) appearance in the soils underlain by serpentinous dunite from the Polar Urals, has been also shown previously (Lessovaia and Polekhovsky [2009](#page-12-0); Lesovaya et al. [2012](#page-13-0)). The saponite–trioctahedral, Mg reach smectite is rare described as a pedogenic mineral. For example, in serpentinite soils in northeast Scotland the saponite, the content of which decreased from the bottom towards the more acidic upper soil horizons was identified (Wilson and Berrow [1978\)](#page-13-0). Based on these findings, the pedogenic origin of saponite in the soils underlain by serpentinous dunite from the Polar Urals was supposed (Lessovaia et al. [2012\)](#page-13-0). The weakly developed soils—Haplic Regosol (Eutric) and Stagnic Leptosol (Eutric) according to the World Reference Base for Soil Resources [\(2006](#page-13-0)) were described here together with more developed soils such as Haplic Cryosols (Reductaquic). The mineral association of the fine size fractions of weakly developed soils characterized by the slightly pronounced pedogenic features was the same as in mature profiles. But the pedogenic origin of saponite supposing the intensive chemical weathering is difficult to explain in weakly developed soils. So, the aim of present research is to investigate the weathering trends of mafic and ultramafic rocks, the origin of phyllosilicate association and the role of abiotic and biotic pedogenic processes in weakly developed soils formed in humid cold climate of the mountainous tundra of the Polar Urals.

2 Objects

The study sites are located at the same altitude of \sim 300 m in the mountainous tundra from the Polar Urals on the southern slope of the Rai-Iz massif and outwith the Rai-Iz massif (Fig. [1\)](#page-2-0). The Rai-Iz massif is mostly consists of the Early Paleozoic dunite–harzburgite ultramafic igneous rocks (harzburgite is peridotite with orthopyroxene) complex, whereas the mafic rocks are adjacent to the Rai-Iz

Fig. 1 Location of the key plot in the Urals

massif (Major Ore-Bearing Geological–Geochemical Systems of the Urals [1990\)](#page-13-0). The landscapes of study area are mainly controlled by glacial landforms formed during Middle Pleistocene glaciation with several distinct moraine lobes around the Rai-Iz massif (Svendsen et al. [2014\)](#page-13-0).

The first study site on the southern slope angled at $\sim 20^{\circ}$ of the Rai-Iz massif covered by colluvial blocks of ultramafic rock determines the formation of well-drained soils in the accumulation of fine earth. The fine earth is a result of redistributed weathering products of ultramafic rock. The surface is covered by the sedge–grass–lichen vegetation community with rare shrubs of blueberry and ledum. Rare trees are represented by larches with the diameter of 8–10 cm, which are not higher than 5 m. Haplic Regosol (Eutric) (WRB [2006\)](#page-13-0) (Pit Y-01-07) was described here.

The second key plot located outwith the Rai-Iz massif, to the north of Lake Yareity, on a moraine ridge. The stoniness of the area is $\sim 60-80$ % with pronounced cryogenic patterned ground. The moraine is greenish-gray and consisted mostly of mafic material with admixture of ultramafic one pointed to erosion and redeposition of Rai-Iz massive igneous rocks. The flat surface determines the development of stagnic features in the bottom of the studied soil profile classified as Stagnic Leptosol (Eutric) (Pit Y-04-07). The surface is covered (70–80 %) by moss–dwarf shrub tundra vegetation community with sedge and rare suppressed larch, dwarf Arctic birch tree (Betula nana), creeping form of willow, blueberry, and ledum. Permafrost was not detected at the pits of the studied area even at the end of June—beginning of July of the year with normal level of precipitation, when

the field research was performed. It is because of the close lithic contact and shallow soil profiles.

Thus, the objects of the study are represented by weakly developed soils formed (i) on and underlain by the ultramafic rock and (ii) on the moraine composed of the mafic rock with an admixture of the ultramafic rock fragments.

3 Methods

Mineral associations of the rock and soil horizons were studied in thin sections by optical microscopy using Zeiss Axioplan 2 and Polam P-312 microscopes. The <1 mm fraction of soil samples was obtained by gently grinding in a mortar and subsequent dry sieving. Bulk chemical composition of the <1 mm fraction and rock was determined by X-ray fluorescence analysis (Tefa-611, EG&G Instruments Ortec). The soluble Fe forms in the fractions <1 mm were obtained from the dithionite citrate bicarbonate method of Mehra and Jackson ([1958\)](#page-13-0) and extractions with oxalate (Jackson et al. [1986\)](#page-12-0), and pyrophosphate (Bascomb [1968](#page-12-0)). In the oxalate extract Al and Si were also analyzed. pH values were measured potentiometrically in H₂O with a soil: water ratio of 1:2.5. C-content of the \leq 1 mm fraction was determined by wet combustion with a mixture of 0.14 M $K_2Cr_2O_7$ and concentrated H₂SO₄ 1:1 at 150 °C for 20 min and titration with ferrous sulfate solution according to Tyurin ([1931\)](#page-13-0). In the A and Ah horizons rich in organic matter, loss on ignition was determined.

The content of the $\langle 1 \rangle$ µm fraction in the fine soil fraction $\langle \langle 1 \rangle$ mm was determined by sedimentation with the pipette method. Ammonium hydrate was used as a peptizing agent. The XRD patterns were obtained from oriented specimens using DRON-2 X-ray diffractometer, with $Cok\alpha$ radiation and a monochromator in the diffracted beam. Pretreatment of samples included saturation with Mg, ethylene glycol solvation, and heating 550 °C. Additionally, FTIR spectra in the 400– 4000 cm−¹ range of the <1 µm fraction were obtained using a Tensor 27 spectrometer (Bruker) with a resolution of 4 cm^{-1} in ambient air and at room temperature. Spectra were recorded in the transmission mode using the KBr pellet method. Here 1 mg of sample and 300 mg of KBr were thoroughly mixed and pressed to a transparent pellet.

4 Results

Rocks characteristic. The rock fragments from soil horizons including bottom one of Haplic Regosol (Eutric), Pit Y-01-07 from the first key plot were identified as serpentinous dunite with predominance of olivine in the mineral association (Fig. [2\)](#page-5-0). Some alteration of initial rock affected by metamorphic processes resulted in appearance of serpentine, talc, and chlorite as well as traces of amphibole and mica.

In the microcracks in olivine, serpentine, and chlorite the accumulation of Fe oxides due to rock weathering leads to a reddening.

The rare boulders of ultramafic rock from the moraine ridge of the second key plot located outside the Rai-Iz massif were also identified as serpentinous dunite. Based on the data of bulk chemical composition the content of $SiO₂$ as well as $A₁Q₃$, and $K₂O$ in the rock fragments from the bottom R horizon of Pit Y-01-07 is higher than it should be in ultramafic rock (Table [1\)](#page-6-0). Supposedly, that could be explained by decrease of proportion of Mg-rich minerals first of all olivine and residual accumulation of possible source of $A₁₂O₃$ and $K₂O₃$.

The rock fragments from the soil profile of Stagnic Leptosol (Eutric), Pit Y-04-07 from the second key study is enriched by total iron and characterized by mafic composition based on the percentage of $SiO₂$ (Table [1\)](#page-6-0). The rock samples from the profile as well as mafic samples from the moraine ridge are identified as metagabbro–amphibolite due to mineral association (Fig. [2\)](#page-5-0). Hornblende predominated in the rock is a result of replacement of pyroxenes all over the rock during high temperature regional metamorphism, which is also caused to recrystallization of some melanocratic minerals in initial rock and appearance of high proportion of quartz. The initial rock was most probably represented by the magmatic type of mafic composition. Later amphibole was partially substituted by epidote and chlorite. Grains of plagioclase are characterized by the development of the saussuritization and sericitization.

In the thin sections from soil horizons of this profile (Pit Y-04-07) the fragments of mafic and ultramafic rocks, which size is up to 10–15 mm illustrate the influence of pyroxenite, serpentinite, metagabbro–amphibolite and epidosite, the latter is composed by epidote (Fig. [2](#page-5-0)). In addition, individual minerals: hornblende, plagioclase and quartz, which size is up to 1.5 mm were also identified. Several rock samples as well as plagioclase and especially pyroxene are characterized by the development of Fe oxides along the cleavages reflecting iron removal from silicates caused to cement soil substrate. Thus, these findings confirm that soil profile of Stagnic Leptosol (Eutric), Pit Y-04-07 is enriched by mafic as well as ultramafic material. As opposed to ultramafic rocks, fragments of mafic one are less weathered based on reddening rims.

Soils' characteristics. The upper horizons (A and Ah) of studied profiles are enriched by total carbon mostly due to the decomposed soil organic matter, not linked with mineral matter that is confirmed by high value of loss on ignition. However, the depth of A horizons is very shallow—2 cm only, in Haplic Regosol (Eutric) the gradient of C content decrease is much higher than in Stagnic Leptosol (Eutric). Haplic Regosol (Eutric), Pit Y-01-07 is alkaline with the exception of the uppermost (A) horizon, whereas Stagnic Leptosol (Eutric), Pit Y-04-07 is neutral in the upper part and slightly alkaline in the bottom horizons despite the absence of calcareous material (Table [1](#page-6-0)).

Higher proportions of Al_2O_3 and especially SiO_2 in the soil horizon of Pit Y-01-07 in comparison with rock samples (R horizon) suppose the influence of allochthonous material. The percentage of MgO in the bulk chemical composition,

Fig. 2 Micromorphology of soil (a, d, e) and rocks (b, c) based on thin sections data: a general view of Bwh horizon, Pit Y-04-07 with fragments of mafic and ultramafic rocks metagabbro–amphibolite (1) , pyroxenite (2), serpentinite (3) , and epidosite (4) ; b sample of metagabbro– amphibolite from Pit Y-04-07; c rock fragment of serpentinous dunite from Pit Y-01-07; d pronounced development of Fe oxides along the cleavages of pyroxene from Bwh horizon, Pit Y-04-07; e weakly (upper) and well developed (down) Fe oxides in grains of pyroxene and fresh grains of plagioclase and serpentine from BC horizon, Pit Y-04-07. Determinations on thin sections at (I) plain polars and (II) crossed nicols. Indexes are due to Whitney and Evans ([2010\)](#page-13-0) in modification: Chl chlorite, Ep—epidote, Ol olivine, Pl—plagioclase, Px —pyroxene, Srp—serpentine; Fe—Fe oxides

bottom of soil profile

Table 1 Some characteristics of studied soils Table 1 Some characteristics of studied soils

especially in the upper horizons of Pit Y-04-07, reflects the influence of ultramafic material; however, the correlation between pH value and the content of MgO is absent. The considerable proportions of the $\lt 1$ μ m fraction in Haplic Regosol (Eutric), Pit Y-01-07, and especially in the bottom horizons of Stagnic Leptosol (Eutric), Pit Y-04-07 demonstrate a sensitivity to the weathering and alteration of parent material of hard rock(s).

Weathering intensity of rock(s) in soil environment is illustrated by oxalate-soluble Si as well as pronounced content of soluble Fe. That is affected by dissolving of Fe-rich minerals and formation of pedogenic Fe oxides. Almost 50 % of soluble Fe, especially in the more developed profile of Stagnic Leptosol (Eutric), Pit Y-04-07 is represented by well-crystallized oxides, whereas the proportion of pyrophosphate extractable Fe, which is related to iron released from the complexes with organic matter, is relatively low. Eluvial–illuvial distribution of dithionite extractable Fe in Pit Y-04-07 also reflects weakly pronounced development of pedogenic processes of podzolization in spite of neutral pH values. In Pit Y-04-07 the soluble Al confirms that the mafic rock is a source of the fine earth taking into account that the portion of Al is extremely low in the ultramafic rock.

Soils' clay mineralogy. The minerals identified in the clay fraction $\left($ <1 μ m) of both profiles are as follows: (i) smectite(s), (ii) serpentine, (iii) chlorite, (iv) talc, (v) mineral of mica group, and (vi) quartz based on XRD data (Figs. [3](#page-8-0) and [4\)](#page-9-0). Smectite(s) is confirmed by a peak at 14.2 Å in the Mg-saturated air-dry state shifts to a fundamental 001 spacing of 17.1 Å after ethylene glycol solvation. As the 002 reflection at 8.6 Å, which is characteristic of a pure smectite, is detected indicating that the expandable phase is represented by individual smectite(s) (Moore and Reynolds [1997\)](#page-13-0). In the studied samples the identification of tri- or dioctahedral nature of smectite(s) due to the 060 (data is not showing) reflection is complicated because of presence of talc, serpentine, chlorite, and a mineral of the mica group. Additional information was due to FTIR data. The absence of OH bending bands in the 950–800 cm−¹ region in the FTIR spectra of clay size fractions points to the absence of dioctahedral coordinated OH groups of smectite (Komadel et al. [2000\)](#page-12-0). The absorption band near 3680 cm^{-1} assigned to stretching vibrations of Mg₃OH (Farmer [1974\)](#page-12-0), the absorption band near 3624 cm⁻¹, ascribed to the $Mg_2Fe^{3+}OH$ vibrations in the spectrum of ferruginous saponite (Farmer [1974\)](#page-12-0), and the absorption band near 533 cm⁻¹ (Si–O–Al bending vibration), documented in the spectrum of saponite (Madejová et al. [1992](#page-13-0)) indicate presence of trioctahedral smectite–saponite in the both profiles. This smectite was also identified previously in the mature profile of Haplic Cryosols (Reductaquic) on serpentinous dunite from mountainous tundra, the Polar Urals (Lessovaia et al. [2012\)](#page-13-0).

Chlorite identification in the presence of smectite(s) is based on the basal reflections at 7.1, 4.72, and 3.57 Å that are stable after ethylene glycol solvation and showing a slight contraction of the 001 peak to 13.8 Å after 550 °C treatment.

Serpentine is recognized in the presence of chlorite by splitting of \sim 7 Å peak at 7.24 (serpentine) and 7.1 Å (chlorite) and presence of 3.64 Å peak.

Talc identification is based on the peaks at 9.3 and 3.12 Å, stable after ethylene glycol solvation and 550 °C treatment. Mineral of mica group is confirmed at the

Fig. 3 XRD patterns (a) and FTIR spectra (b) of the $\lt 1$ µm fraction of the soil horizons, Pit Y-01-07

001 and 002 basal reflections at 10.0 and 5.0 Å, respectively, that remain stable after ethylene glycol and heat treatment.

Quartz is identified by its characteristic XRD peaks at 3.34 and 4.26 Å and by its most typical IR absorption band doublet at 800–780 cm^{-1} (Hlavay et al. [1978;](#page-12-0) Madejová and Komadel [2005](#page-13-0)).

Absence of absorption bands near 3700 cm−¹ (the vibration of inner surface OH groups), as well as 914 cm^{-1} (bending vibration of inner OH groups) indicates that kaolinite is not identified in the soil profiles (Madejová and Komadel [2001](#page-13-0); Pentrak et al. [2009\)](#page-13-0). So, kaolinite does not affect the \sim 7 and 3.5 Å peaks confirmed by

Fig. 4 XRD patterns (a) and FTIR spectra (b) of the $\lt 1$ µm fraction of the soil horizons, Pit Y-04-07

FTIR spectroscopy data, which is more sensitive method for the detection of kaolinite (Delvaux et al. [1989](#page-12-0)).

The distribution of the clay minerals in the profile based on mentioned above criteria is characterized by slightly decrease of smectite portion in the upper horizons, which is more pronounced in Pit Y-04-07. Proportion of chlorite based on peak intensity is higher in Pit Y-01-07.

5 Discussion

The origin of the allochthonous material supposed by proportions of $SiO₂$ and $A₁O₃$ in Haplic Regosol (Eutric), Pit Y-01-07 could be related to eolian or water transfer. Nevertheless, the strong affect of ultramafic rock is pronounced based on MgO percentage. In Stagnic Leptosol (Eutric), Pit Y-04-07 the influence of ultramafic rock is concluded based on MgO proportion in the bulk chemical composition, especially in the upper horizons. The increase of $SiO₂$ percentage in the soil fine earth (the ≤ 1 mm fraction) in comparison with rock samples (R horizon) is most probably a result of the residual accumulation of inherited quartz, which content is high in metagabbro–amphibolite. Based on these findings BC and BCg are mostly affected by mafic rock.

High pH values in Haplic Regosol (Eutric), Pit Y-01-07 is mostly assigned by ultramafic material. Ultramafic rock resulted in soil alkalinity in spite of the absence of calcite keeping by high amounts of exchangeable Mg, which was shown previously (Lesovaya et al. [2012\)](#page-13-0). pH values in Stagnic Leptosol (Eutric), Pit Y-04-07, which are higher than in the mature profile of Epileptic Entic Podzols on metagabbro–amphibolite (Lessovaia et al. [2014](#page-13-0) in press) is also affected by ultramafic substrate.

Both profiles are characterized by poorly developed organic horizons (2 cm in depth) of the decayed organic material mixed with mineral mass. Stagnic Leptosol (Eutric), Pit Y-04-07 on the moraine has more developed organic profile with higher content of organic C in Bwh horizon. That is related to more toxic conditions in case of ultramafic material. The problem is also in the absolutely different roles of ultramafic and mafic rocks in the ecosystems and soil development—strongly deteriorative one in first case (Alexander et al. [2007](#page-12-0)) but usually enriching one in case of basic material (Lal [2006\)](#page-12-0). However, the outcrops of ultramafic rocks are used to be adjacent in space to the mafic rocks (Kusky [2005\)](#page-12-0) but study of soils and weathering trends of this transition in cold environment is still poorly known.

A sensitivity to weathering and alteration of the parent materials based on the proportion of <1 μm fraction is confirmed by pronounced reddening of ultramafic rock fragments and proportions of soluble forms of Si, Al, and especially Fe. Iron removal from silicates matrix, especially the fine-grained parent rocks is reflected by increase of dithionite—and, oxalate extractable iron, that is more pronounced in the upper part of Pit Y-04-07. Here in Bwh horizon thin films of Fe–Al-organo complexes on stones were found. Previously, the development of weathering rinds, in which the weathering is isolated from other soil processes was detected (Colman [1982\)](#page-12-0). These findings indicate the translocation of poorly crystalline iron and aluminum oxides, although the studied soil is characterized by neutral pH values most probably due to podzolization. However, the admixture of ultramafic materials mitigates the development of Entic Podzols which were found in the Polar Urals on the pure mafic materials (Lessovaia and Polekhovsky [2009\)](#page-12-0). Based on the findings of thin section from soil horizons of this profile, we can conclude that the source of iron coursed the reddening rims of rock fragments is ultramafic substrate. Generally, the sensitivity of ultramafic rocks to weathering can strongly influence not only soil macrofeatures but also landscape stability (Alexander [2009](#page-12-0); Alexander and DuShey [2011\)](#page-12-0). Thus, the features affected by chemical weathering are obvious in the weakly developed soils.

The identity of mineral associations of clay size fraction from both profiles confirms that the soils are characterized by the same sources of them. Talc and serpentine are definitely affected by ultramafic substrate. Chlorite is also inherited from ultramafic substrate based on its presence in serpentinous dunite. Additionally, the presence of chlorite as well as mica and quartz in Stagnic Leptosols (Eutric), Pit Y-04-07 can be affected by metagabbro–amphibolite. Whereas mica and quartz in Haplic Regosol (Eutric), Pit Y-01-07 are allochthonous. The presence of quartz here can explain the high proportion of $SiO₂$ in the profile.

The smectite identified as saponite from both studied profiles is absent in the rocks of serpentinous dunite as well as in metagabbro–amphibolite. Generally, the smectite appeared in the soils could be a result of the crystallization caused by weathering of (i) amphibole, which was detected in metagabbro–amphibolite (Proust et al. [2006;](#page-13-0) Wilson and Farmer [1970](#page-13-0)) or (ii) olivine (Bulmer [1992;](#page-12-0) Eggleton [1984;](#page-12-0) Wilson [2004](#page-13-0)) and/or transformation of serpentine from serpentinous dunite. But previously the smectite was identified only in Haplic Cryosols (Reductaquic) on serpentinous dunite but not in Entic Podzols on metagabbro–amphibolite (Lessovaia and Polekhovsky [2009](#page-12-0)). Thus, the appearance of smectite in the weakly developed profiles can be affected by the weathering only of ultramafic rock. In Stagnic Leptosols (Eutric), Pit Y-04-07 influenced by mafic and ultramafic rocks the proportion of smectite in clay size fraction does not correlate to the percentages of MgO or $SiO₂$ which can be explained that smectite is located in fine size fractions, whereas proportions of oxides characterize the bulk chemical composition (<1 mm). Besides that, the main source of Mg in the ultramafic rock is olivine concentrated in the course fractions.

Generally, the processes affected by only pedogenesis could not be split from ones influenced by chemical processes. Nevertheless as opposed to the studied weakly developed profiles, in the more mature profile of the Haplic Cryosol (Reductaquic) on serpentinous dunite the pedogenesis resulted in significant decrease of proportion of smectite and the appearance of vermiculite due to chlorite transformation in the upper horizons (Lessovaia et al. [2012\)](#page-13-0). Thus, it can be concluded that the appearance of smectite (saponite) in the weakly developed soils is not related to pedogenesis. These soil profiles illustrate the soil formation from "mature" fine earth from high-sensitive ultramafic rock due to chemical weathering.

6 Conclusion

In cold soil environment the more weatherable ultramafic material plays the more important role as a prerequisite for the weathering trends and soil formation than a mafic rock.

Appearance of smectite in the weakly developed soil profiles illustrates the scenario of soil formation slightly affected by pedogenic biotic processes, but from the "mature" fine earth due to the active abiotic chemical weathering in the cold region.

The admixture of ultramafic materials mitigates the development of Entic Podzols which were earlier found in the Polar Urals on the pure mafic materials. So, the presence of ultramafic materials either predominating or even in admixture results in the "extreme lithological environment" for a pedogenesis and in the formation of weakly developed soils—Regosols and Leptosols.

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