Smectites in soils from serpentinous dunites of the Polar Urals, Russia

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Introduction

Olivine is not a stable mineral in soil environment because of extreme susceptibility to weathering, especially in acidic conditions. Saponite and goethite identified in iddingsite rims on olivine were reported as a result of weathering (Eggleton 1984). During the first stages of olivine weathering trioctahedral smectites are formed and subsequently may have been replaced by dioctahedral smectites (nontronite-beidellite) (Wilson 2004). Our previous study (Lessovaia and Polekhovsky 2009) identified smectite supposedly saponite in mineral association of shallow stony solum from serpentinous dunites in the Polar Urals, Russia. The aims of present research is to identify the features of smectite or smectite association from shallow soil derived from an underling serpentinous dunite located in mountainous tundra of the Polar Urals, Russia on the basis of XRD, IR spectroscopy, and thermal analysis.

Study Location

The key plot is located in mountainous tundra, on a flat summit (altitude is 664m) of the Polar Urals where dunite - harzburgite (peridotite with orthopyroxene) complex makes up the Rai-Iz massif. Climate conditions are characterized by mean annual temperature -9.0ºC and precipitation 800 mm. The soils are represented by stony, shallow Haplic Cryosols (Reductaquic) (World Reference Base for Soil Resources, 2006); permafrost is at a depth of 30 cm. Crushed stones and gravels are made up by ~ 70% of the total volume in solum. The sequence of horizons is Ah 0-4 cm – Bg 4-15 cm – Bgf 15-30 cm – R.

Methods

The hard rocks and soils horizons were studied in thin section by optical microscopy using Zeiss Axioplan 2 and Polam P-312 microscopes. The fine size fraction of the soils ($<1\mu m$) was obtained by sedimentation. Ammonium hydrate was used as a peptizing agent. The XRD patterns were obtained using D/MAX-2200 X-ray diffractometer (Rigaku, Cu-$K\alpha$ radiation). Pretreatment of samples included (i) saturation with Mg, Li, and K; (ii) heating at 350ºC and 550ºC; and (iii) ethylene glycol solvation. Li-saturated samples were heated at 250^0C for 12 h and solvated by ethylene glycol according to procedure of Greene-Kelly test. Derivative thermogravimetry was carried out using thermoanalyser Q-1500D from room temperature to 1000^oC. Infrared absorption (IR) spectra were obtained on a Fourier spectrometer FMS-1201with petrolatum oil from 400 - 4000 cm^{-1} at room

temperature (air-dried and 400°C heated samples), frequency accuracy was about 1cm^{-1}. Bulk chemical composition was done by X-ray fluorescence analysis. Various forms of Fe and Al were received on the base of dithionite (Mehra and Jackson treatment), oxalate, and pyrophosphate extractable procedures. The pH values were measured potentiometrically in the suspension with a soil:H_2O ratio of 1:2.5 (shaking for 2 h).

Results and discussion

A short list of the analytical characteristics of soil is given in Table 1. The studied solum is loamy - clayey loamy in the basal horizon, pH- neutral in the upper and alkaline in the basal horizon keeping by high amounts of exchangeable Mg.

Table 1. Some properties of studied solum.

Horizon, depth (cm)	pH H_2O	<1µm %*	Bulk content of some elements, % in ignited sample							Fe_2O_3			Al_2O_3
			SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	d	o	p	o
											%		
Haplic Cryosols (Reductaquic), Pit. Y-02-07													
Ah 0-4	7.2	7.8	54.59	5.05	10.62	1.35	25.88	0.75	0.63	2.68	1.79	0.14	0.08
Bg 4-15	7.0	6.8	56.00	5.70	11.25	1.43	22.57	0.86	0.96	4.05	2.57	0.24	0.11
Bgf 15-30	8.0	17.4	65.92	8.66	7.10	1.44	13.23	1.35	1.20	1.53	0.66	0.04	0.11
R	–	–	44.52	0.72	12.87	0.85	40.34	0.10	trace	–	–	–	–
stones **	–	–	44.40	0.90	13.39	0.89	39.86	0.05	trace	–	–	–	–

Notes: d – dithionite, o - oxalate, and p - pyrophosphate extractable; «–» - no data; * - content of fraction <1µm, %; ** - stones from the surface of permafrost circle.

Rock and stone samples from the solum are represented by serpentinous dunites, which was concluded on the basis of thin section study. The olivine grains are broken into fragments and may be replaced by serpentines, talc, and chlorites. Occasional flakes of magnesian micas also occur, often chloritized as well as serpentine. In solum iron (hydr)oxides fill in micro-cracks of olivine, pyroxenes, and serpentine, especially in Bg 4-15 horizon (Fig. 1).

Dispersed minerals, especially olivine, are likely to be a source for iron (hydr)oxides. Iron removal from silicates matrix is reflected by increase of dithionite - and, especially oxalate extractable forms. Content of pyrophosphate extractable iron connected with organic matter is very low. Pyroxenes are not identified in thin sections of rock samples; probably their source for solum is harzburgite. Olivine, talc, chlorite, serpentine and amphiboles are detected in powder of stones on the basis of XRD data. The fine earth of even basal horizon of soil is characterized by (i) dramatic decrease of olivine and (ii) some amount of quartz and feldspars as a result of allochthonous material influence (probably by eolian transfer) and illite. Smectite presence in the fraction < 1µm of solum is confirmed by a peak at 14.4 Å (Mg-saturated samples), which shifts to 16.7 Å after ethylene glycol solvation and the appearance of a peak at 8.6 Å (Fig.2).
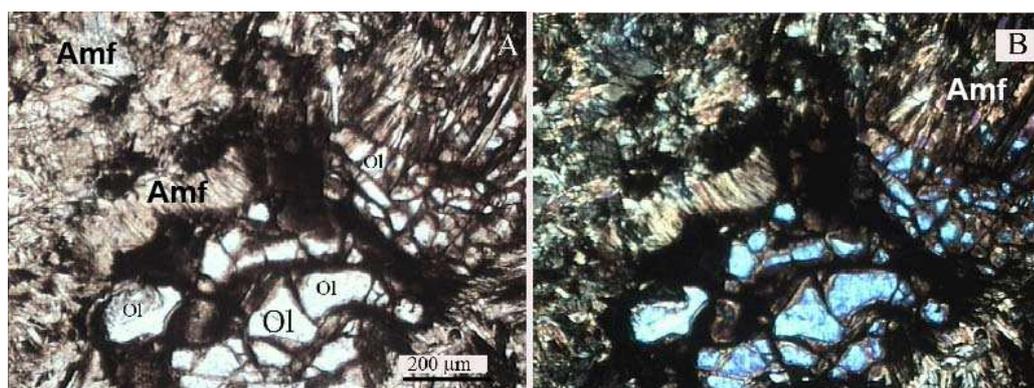
Fig.1. Broken olivine grain (Ol) and amphibole (Amf); A – plain polars, B –crossed nicols; Bg 4-15cm horizon.
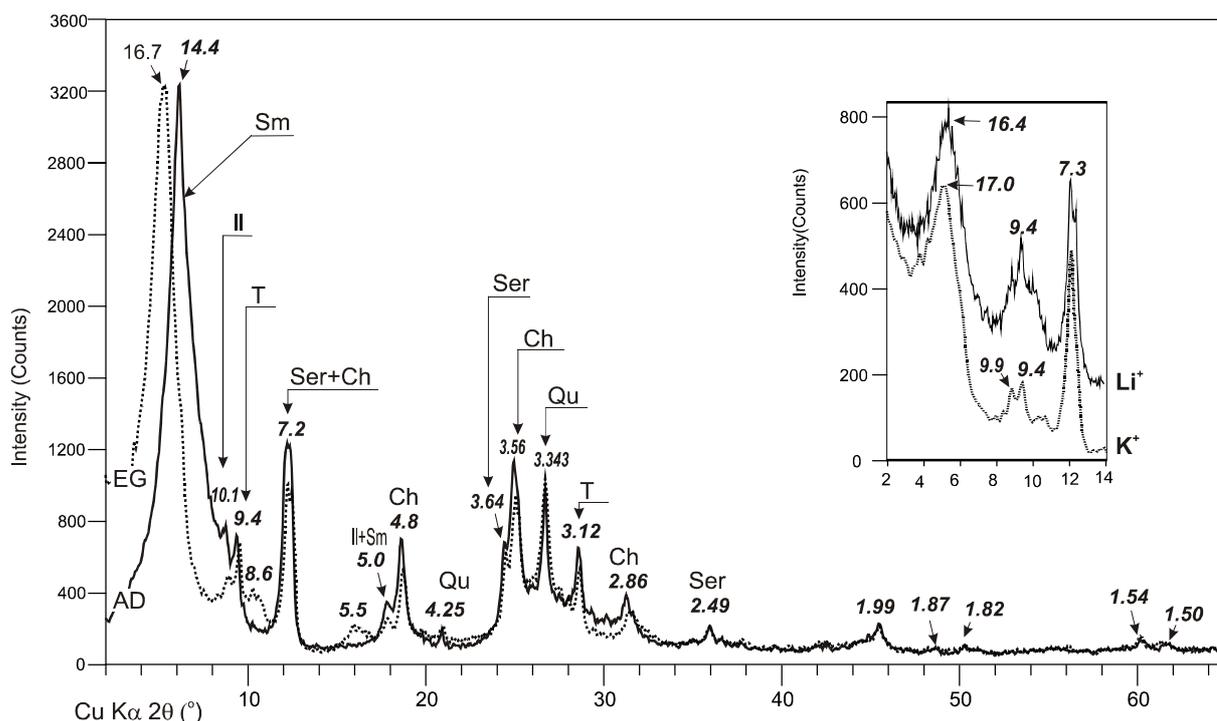
Fig.2. XRD patterns of fraction < 1µm (horizon Bgf 15-30), oriented sample: Mg-saturated (AD), and ethylene glycol solvated (EG); K-saturated and ethylene glycol solvated (K^+) and Li-saturated and ethylene glycol solvated after heating (250^oC, 12 h) (Li^+) in a separate box. Minerals: smectite (Sm), serpentine (Ser), chlorite (Ch), talc (T), illite (Il), and quartz (Qu).

Li-saturated samples illustrate swelling properties of smectite after heating and ethylene glycol solvation and thereby charge location in the tetrahedral sheets (Moore and Reynolds 1997).

K-saturated samples show the basal smectite peak location at 12.9 Å and 17 Å after ethylene glycol solvation that could be corresponded to saponite (Suquet *et al* 1975) and characterizes small total layer charge (Christidis and Eberl 2003). In the studied samples the 060 reflections do not allow the distinction between di- and trioctahedral smectites because of the presence of illite, talc, serpentine, and chlorite.

IR absorption spectra (fractions <1µm) allow to suggest the presence of two minerals of smectite group: (i) nontronite identified on the basis of absorption at the wave numbers near 3586 and 820 cm^{-1} (FeFeOH) and 670 cm^{-1} (Fe-O out-of-plane); and (ii) saponite on the basis of absorption at the wave number near 3686 cm^{-1} (Mg_3OH) (Madejova and Komadel 2005). Results of thermal analysis

illustrate (Table 2) mass loss due to (I) adsorption water; (II) oxidation and burning of organic matter; and (III) dehydroxylation of: nontronite (t_{max} 500 ^{o}C for Ah 0-4 and 530°C for Bgf) and saponite (t_{max} 600°C and 630°C for Ah 0-4 and Bgf 15-30, correspondently). These peak maximums are lower than expected to occur for saponite. But temperature of endothermic peak can decrease as a result of crystallinity decrease of mineral (Bish and Duffy 1990) that suggests the presence of saponite whose poor crystallinity is due to its pedogenic origin. Thus, two smectites are also illustrated by this method.

Table 2. Thermal analysis data (<1µm fraction)

Horizon, depth, cm	I step			II step			III step			Total
	interval, ^{o}C	t_{max}, ^{o}C	mass loss, %	interval, ^{o}C	t_{max}, ^{o}C	mass loss, %	interval, ^{o}C	t_{max}, ^{o}C	mass loss, %	mass %
Ah 0-4	70-200	125	7.1	200-350	270	14.9	350-800	440, 500, 600	9.0	31.0
Bgf 15-30	70-200	125	6.6	200-450	330	5.3	450-800	530, 630	6.9	18.8

Conclusion

Two minerals of smectite group – saponite and nontronite are identified in solum derived from and underline serpentinous dunites using a suite of methods. Saponite is the most probably the result of magnesian silicates transformation. The pronounced disintegration and iron (hydr)oxides formation in solum could be explained by permafrost influence leading to increase of silicate dispersion with consequent transformation/ decomposition, especially olivine as one of the most unstable mineral. The question is the source of nontronite: (i) olivine or other magnesian silicates from serpentinous dunites as well as for saponite, or (ii) pyroxenes inherited from harzburgite affecting solum mineral association. The amount of smectites markedly decreases in the upper horizon in spite of pH value in bulk samples without appearance of new transformation phases.

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