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CHARACTERIZATION OF SERPENTINE SOILS FROM EASTERN AND SOUTHERN RHODOPE MOUNTAINS (BULGARIA)

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Abstract

This work aims to characterize serpentine soils in Bulgaria and examine the biogeochemistry of pedogenic Ni and its relation to Ni available forms. Soils were collected from serpentine soils of the Eastern and Southern Rhodopes (Bulgaria). The chemical composition of serpentine soils is similar to serpentine soils from the Balkan Peninsula and is characterized by high contents of Ni (919.9–2397.2 mg.kg^{-1}). The soils had a neutral to slightly alkaline reaction (pH 6.4 to 7.6) and a medium to high organic matter content. Of the primary minerals, those of the serpentine group (antigorite and lizardite), the talc group (willemseite), the amphibole group (riebeckite), the feldspar group (albite) and quartz are mainly present in the soil samples. The secondary minerals present in the samples include calcite and dolomite, and also representatives of the clay minerals, clinochlore and montmorillonite. The contents of free iron oxides (Fed), amorphous iron oxides (Feo), well-crystallized iron oxides (Fecr) (Fed-Feo) and activity index (Feo/Fed) showed significant differences ($p < 0.05$) among soils from different locations. In the soils from Dobromirtsi, Parvenets, and Golyamo Kamenyane Ni bound to Fe oxides were evenly distributed between the well-crystallized and amorphous phases. In the soils from Kardzhali, Chernichevo and Dyulitsa more than half of the Ni bound to Fe oxides were bound to or occluded in amorphous Fe oxides, while in the soils from Kazak

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were bound to well-crystallized Fe oxides. Pedogenesis, weathering intensity, and Fe geochemistry influence Ni availability in serpentine soils.

Key words: availability, nickel, Fe geochemistry

Introduction. Serpentine soils are widespread in the Balkan region. They are also found in Bulgaria, mostly in the Eastern and Southern Rhodope Mountains. Serpentine soils originate from serpentine rocks, which are usually shallow, and have specific physical and chemical properties, such as low nutrient status, cation imbalance, low Ca/Mg ratio, moisture stress, soil instability, high surface temperature and high metal contents such as Ni, Co and Cr.

The main sources of geogenic nickel in serpentine soils are primary minerals such as pyroxene, olivine, spinel, amphibole, and serpentine minerals such as chrysotile and antigorite [1, 2]. Chemical weathering of Ni-bearing minerals results in the release of Ni [1]. The intensity of this process varies greatly during pedogenesis depending on climate and influences the formation of new minerals [3]. Released Ni can be adsorbed onto the surfaces of newly formed secondary clay minerals (smectite or vermiculite), incorporated into their lattices and replaced with Mg or bound to Fe-Mn oxides [4, 5].

Fe oxides from different crystallization stages are also considered important Ni carriers, especially in surface soil horizons [6]. The availability of Ni in primary minerals and primary clay minerals (i.e. serpentine minerals) is deficient due to Ni retention in crystal lattices. However, some high solubility can be observed due to the slight weathering of these minerals and the lack of secondary minerals with a high charge for further resorption [3].

It is believed that the most critical factor determining the availability of Ni in serpentine soils is the carrier phases, respectively, the minerals with which Ni is associated. Although pH is the factor that most influences the solubility of Ni in soils [7], the availability of Ni in serpentine soils depends on the mineralogy and nature of the Ni-bearing phases [6, 8].

This work aims to characterize serpentine soils in Bulgaria, and to examine biogeochemistry of pedogenic Ni in serpentine soil and its relation to Ni available forms.

Materials and methods. Soils were collected from the surface soil horizon (0–20 cm) of the Eastern and Southern Rhodopes (Bulgaria) (in the vicinity of Kazak, Golyamo Kamenyane, Avren, Chernichevo, Kardzhali, Fotinovo, Dyulitsa, Dobromirtsi, Asenovgrad, Cherven, Parvenets and Gornoslav). Soils were dried to an air-dry state and sieved through a 2 cm^2 sieve. pH of soils was determined according to ISO 10390 [9], organic matter according to BDS EN 13039 [10]. The total nickel content was extracted with aqua water according to ISO 11466 [11] and DTPA-extracted mobile forms of nickel according to ISO 14870 [12], Cation-exchange capacity (CEC) and exchangeable cations were determined with 0.1 M $BaCl_2$ solution [13]. Amorphous iron oxides (Feo) were extracted with ammonium oxalate solution and pedogenic crystalline iron oxides and non-crystalline iron oxides (Fed) with dithionite solution [14]. The elemental contents of the samples were determined by plasma emission spectrometry (ICP-OES, Prodigy 7).

XRD analysis was used to determine the mineral composition of the soils. Powder X-ray diffraction patterns were recorded in the angular range from 5.3 to 80o2θ with a constant step of 0.02 o2θ on a Bruker D8 Advance diffractometer with Cu Kα radiation and a LynxEye detector. Phase identification was performed with the Diffracplus EVA program using the ICDD-PDF2 database. Phase quantification by the Rietveld method was performed with the Topas-4.2 software package.

The SPSS for Windows program was used in the statistical processing of the data.

Results. Table 1 presents the results obtained for pH, organic matter, cation-exchange capacity, ratio of exchangeable magnesium and calcium ions, DTPA mobile forms of Ni and Ni total content in the studied soils. The chemical com-

Table 1

Chemical composition of serpentine soils

Point	Soil sample	pH	Organic matter, %	CEC, mmolc.kg^{-1}	Mg/Ca ratio	Ni DTPA, mg.kg^{-1}	Ni total, mg.kg^{-1}
Kazak	3	6.3	7.24	189.4	0.8	90.6	1597.3
Kazak	62	6.8	7.30	155.7	0.8	99.4	1481.3
Kazak	64	6.1	6.74	204.7	1.2	125.3	1365.1
Kardzhali	6	7.6	5.41	270.6	0.4	13.4	1708.9
Dobromirtsi	7	7.6	3.22	163.8	2.6	47.1	1553.7
Fotinovo	10	6.5	2.69	242.4	1.3	50.5	919.9
Chernichevo	23	7.0	6.81	252.5	1.3	92.2	1319.9
Chernichevo	32	6.6	3.04	197.3	3.4	55.5	2205.9
Avren	30	7.1	2.27	243.8	1.3	30.7	1439.0
G. Kamenyane	59	6.2	6.82	243.8	1.3	64.5	1610.4
G. Kamenyane	60	6.4	4.57	310.6	1.9	48.7	2122.5
G. Kamenyane	63	6.6	3.35	434.5	3.1	30.4	2397.2
Parvenets	11	6.9	8.30	207.2	1.4	17.1	1297.5
Parvenets	37	7.6	4.01	110.2	0.8	12.0	2277.6
Asenovgrad	57	7.6	7.13	166.7	0.4	24.9	1655.0
Cherven	54	7.1	6.34	409.4	0.1	14.9	1547.2
Gornoslav	43	7.2	5.05	131.6	1.3	33.2	2228.3
Dyulitsa	68	6.8	3.69	198.5	4.7	27.6	1678.4
Dyulitsa	69	6.3	4.33	196.4	2.2	55.2	1676.6
Dobromirtsi	78	6.5	7.16	83.1	2.1	6.1	1276.1

position of serpentine soils from the Eastern and Southern Rhodopes is similar to serpentine soils from the Balkan Peninsula. It is characterized by high Ni content (912–2397 mg.kg^{-1}) and low to medium DTPA Ni content (13.4–125.3 mg.kg^{-1}). The pH values range from 6.4 to 7.6, and the amount of organic matter from 2.27 to 8.30%. Their cation-exchange capacity is low to medium. The lowest CEC value of 110.2 mmolc.kg^{-1} was found in sample Parvenets (soil 37) and the highest value of 434.5 mmolc.kg^{-1} in sample Golyamo Kamenyane (soil 63). The highest values of Mg/Ca ratio were found in the samples from Dyulitsa (soil 68) (4.66), in the samples from Kazak (soil 64), Dobromirtsi (soil 7), Fotinovo (soil 10), Chernichevo (soil 23), Avren (soil 30), and Golyamo Kamenyane (soils 59 and 60) it varies within the range of 1.20 to 3.36, while in the samples from Kazak (soils 3 and 62) and Kardzhali (soil 6) the ratio is less than 1.

Table 2 shows the resulting mineral composition of the soils from the XDR

Table 2

Minerals in soil samples determined by X-ray diffraction

Soil sample	Minerals, %									
	Ant	Will	Clino	Mont	Quartz	Rieb	Albite	Calc	Dolom	Liz
3	65	10	10	nd	11	6	nd	nd	nd	nd
62	67	10	8	nd	8	7	nd	nd	nd	nd
64	72	nd	16	nd	3	9	nd	nd	nd	nd
6	76	nd	nd	< 1	13	nd	nd	6	5	nd
7	71	6	8	nd	10	5	10	nd	nd	nd
10	19	13	24	nd	13	nd	17	nd	nd	nd
23	51	16	23	9	10	21	nd	nd	nd	nd
32	73	13	13	nd	1	16	nd	nd	nd	nd
30	72	10	18	nd	< 1	1	nd	nd	nd	nd
59	65	3	19	nd	2	< 1	nd	nd	nd	nd
60	65	nd	15	nd	3	< 1	nd	nd	nd	nd
63	35	3	48	nd	6	11	nd	nd	nd	nd
11	19	13	24	nd	13	21	17	nd	nd	nd
37	80	nd	nd	nd	< 1	8	nd	nd	nd	20
57	70	24	nd	nd	3	16	nd	nd	3	nd
54	40	< 1	nd	5	55	6	nd	nd	nd	nd
43	86	nd	2	1	< 1	7	nd	nd	nd	11
68	86	nd	6	nd	8	9	nd	nd	nd	nd
69	62	11	8	nd	14	nd	3	nd	nd	nd
78	37	7	12	nd	13	5	10	nd	nd	nd

Minerals: Antigorite (Ant), Willemseite (Will), Clinochlore (Clino), Montmorillonite (Mont), Quartz, Riebeckite (Rieb), Albite, Calcite (Calc), Dolomite (Dolom), Lizardite (Liz) nd-not detectable

Table 3

Content of Fe and Ni in soil samples after extraction with ammonium-oxalate (Feo, Nio) and citrate-bicarbonate-dithionite (Fed, Nid) and activity index (Feo /Fed)

Soil	Fe o, mg.kg^{-1}	Fe d, mg.kg^{-1}	Index Feo /Fed	Ni o, mg.kg^{-1}	Ni d, mg.kg^{-1}	Nio/Nid
3	4132.5	41096.3	0.10	499.5	583.8	0.86
62	4585.5	34306.3	0.13	508.5	528.8	0.96
64	5641.5	39552.5	0.14	492.0	463.8	1.06
6	2812.5	11837.5	0.24	175.5	87.5	2.01
7	3793.5	29732.5	0.13	348.0	343.8	1.01
10	3261.0	12953.8	0.25	175.5	130.0	1.35
23	5413.5	24898.8	0.22	496.5	321.3	1.55
32	5653.5	23347.5	0.24	646.5	526.3	1.23
30	2515.5	21938.8	0.11	303.0	357.5	0.85
59	2673.0	9535.0	0.28	250.5	245.0	1.02
60	6552.0	20296.3	0.32	538.5	445.0	1.21
63	5742.0	9362.5	0.61	667.5	408.8	1.63
11	2197.5	12283.8	0.18	103.5	61.3	1.69
37	2983.5	14740.0	0.20	363.0	350.0	1.04
57	4200.0	3318.8	1.27	243.0	77.5	3.14
54	2467.5	28173.8	0.09	196.5	482.5	0.41
43	1512.0	7198.8	0.21	579.0	428.8	1.35
68	6177.0	12576.3	0.49	501.0	295.0	1.70
69	4669.5	12526.3	0.37	549.0	306.3	1.79
78	6094.5	18167.5	0.34	330.0	273.8	1.21

analysis. Of the primary minerals, those of the serpentine group (antigorite $(Mg,Fe,Ni)_3Si_2O_5(OH)_4$) and lizardite ($Mg_3(Si_2O_5)(OH)_4$) are mainly present in the soil samples,) from the talc group (willemseite $(Ni,Mg)_3Si_4O_{10}(OH)_2$), from the amphibole group (riebeckite, $Na_2(Fe^{2+}_3Fe^{3+}_2)Si_8O_{22}(OH)$, from the feldspar group (albite $NaAlSi_3O_8$) and quartz SiO_2. Secondary minerals present in the samples include calcite $CaCO_3$ and dolomite $CaMg(CO_3)_2$, as well as representatives of the clay minerals, clinochlore $Mg_5Al(AlSi_3O_{10})(OH)_8$ and montmorillonite $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_{2-n}H_2O$.

Table 3 presents the results obtained for free iron oxide (Fed), amorphous iron oxide (Feo) and well-crystallized iron oxide (Fed-Feo) contents, which provide information on the degree of Fe oxide crystallization and the degree of soil development.

Discussion. According to Bani et al. [15], the availability of Ni depends on the soil genesis. Temperate serpentine soils contain primary "serpentine" minerals (chrysotile, antigorite, lizardite) and secondary phyllosilicates (smectite, magnetite, chlorite, talc) [6]. In all soil samples studied, the main mineral component was antigorite (a silicate mineral of the serpentine mineral group) with a content between 19% (Parvenets, soil 11) and 86% (Gornoslav, soil 43 and Dyulitsa, soil 68). Lizardite (a silicate mineral of the serpentine mineral group) was also found in the samples from Gornoslav (soils 43 and 37). Most of the samples contained wilemseite (a mineral of the talc group), which reached 24% (Asenovgrad, soil 57). The majority of the samples contain ribekite (amphibole group mineral), which reaches 16% (Fotinovo, soil 10) and 21% (Golyamo Kamenyane, soil 60). Quartz was found in almost all samples, with the highest contents in Cherven (soil 54, 55%). Calcite was detected in Kardzhali (soil 6, 6%), while dolomite was detected only in Kardzhali (soil 6, 5%) and Asenovgrad (soil 57, 3%). The clay mineral content reaches 48% (Golyamo Kamenyane, soil 63).

The major minerals found in soils of the serpentine group (antigorite, lizardite) and minerals of the chlorite group (clinochlorite) are not stable in soil environments [16]. Serpentines are known to weather smectite during pedogenesis, whereas chlorite weathers to vermiculite before becoming smectite [17]. As these minerals are still major components of the mineral composition, the soils of the present study can be assessed as being relatively early in development and moderately weathered.

According to Blume and Schwertmann [18], the crystallization of iron oxides in soils is a fundamental process of soil genesis, and the Feo/Fed ratio ("activity index") is used as a relative measure of the extent of ageing of free Fe oxides. The amorphous Fe oxide content is relatively low (less than 10%) and ranges from 2.93% in soil 11 (Parvenets) to 9.75% in soil 60 (Golyamo Kamenyane) of the total Fe content (Table 3). Free and well-crystallized iron oxides constitute a high percentage of the total Fe content in soils and reach 55.2% and 47%, respectively, (Kazak, soil 64). The activity index (Feo/Fed) ranged from 1.27 in soil 57 (Asenovgrad) to 0.1 in soil 3 (Kazak). It can be concluded that soil from Asenovgrad is the least weathered and least developed soil. Soil 3 from Kazak shows progress in its development and intensity of weathering, being the most developed, with the highest concentration of well-crystallized iron oxides (36063.8 mg/kg) and low activity (0.1).

Although free Fe in soils is predominantly under well-crystallized forms, Ni is associated with well-crystallized and amorphous Fe-oxides. In samples from Kazak (soils 62 and 64), Dobromirtsi (soil 7), Parvenets (soil 37) and Golyamo Kamenyane (soil 59), Ni bound to Fe oxides were evenly distributed between the well-crystallized and amorphous phases, as the Nio:Nid ratios were approximately 1. In the samples from Kardzhali (soil 6), Fotinovo (soil 10), Chernichevo (soils 23 and 32), Golyamo Kamenyane (soils 60 and 63), Parvenets (soil 11), Avren (soil 57), Gornoslav (soil 43) and Dyulitsa (soil 68) the Nio:Nid is higher than 1, which means that more than half of the Ni bound to Fe oxides is bound to or occluded in amorphous Fe oxides. While in the samples from Kazak (soil 3), Avren (soil 30) and Cherven (soil 54), the Nio: Nid ratio is less than 1, which means that more than half of the Ni is bound to the well crystallized Fe oxides.

According to references [1, 6, 15, 16, 19, 20], the availability of Ni in serpentine soils depends on the amount of free Fe, and the fraction of Ni adsorbed to amorphous Fe-oxides. The results show that a significant fraction of total Ni is bound to free Fe-oxides (2.9–39.4%) and amorphous Fe-oxides (8.0–37.6%). Ni is primarily bound to amorphous Fe oxides rather than incorporated into the lattices of well-crystallized Fe oxides since the Nio:Nid ratio is higher than Feo:Fed. Because Fe oxide crystallization and Ni partitioning among Fe oxides depend on soil age and weathering, Ni availability is related to weathering intensity and pedogenic processes. According to ECHEVARRIA et al. [3], Ni availability is higher in moderately weathered soils where Ni is associated with poorly crystallized phyllosilicates, clay minerals and amorphous Fe-oxides, which is confirmed by results from this study.

Conclusions. Pedogenesis, weathering intensity and Fe geochemistry influence Ni availability in serpentine soils. The serpentine soils from the Eastern and Southern Rhodopes are at an early stage of development and are moderately weathered. The soils are characterized by low to medium CEC values dominated by Mg, high Ni content (919.2–2397.2 mg.kg^{-1}) and low to medium DTPA Ni content (13.4–125.3 mg.kg^{-1}). Up to 10% of total Ni may be available to plants, with Ni availability controlled mainly by amorphous/poorly crystallized Fe-oxides.

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