



Mobility of Ni, Cr and Co in serpentine soils derived on various ultrabasic bedrocks under temperate climate



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ABSTRACT

Serpentine soil is a common name for soils derived either from igneous peridotites or metamorphic serpentinites. However, differences in mineralogy of these rocks are responsible for some differences between soils occurring on peridotites and serpentinites. In this study, we analyze the mobility of Ni, Cr and Co in six serpentine sites derived from a variety of parent substrates: from partially serpentinized peridotites through serpentinites containing relics of primary minerals and textures to proper serpentinites. The mobility of Ni, Cr and Co, determined using the EDTA extraction, is the highest for Ni whereas Cr is the least mobile element in all soils studied. No relationship between type of parent rock and Cr mobility is found. The lowest proportions of EDTA extractable fractions of Ni and Co (up to 7 and 4% of total concentrations, respectively) are observed in soils derived from proper serpentinites devoid of primary minerals (e.g., olivine, pyroxene) and having non-pseudomorphic texture. The highest proportions of EDTA extractable Ni and Co are noted in soils derived from partially serpentinized peridotite, hornblende peridotite and serpentinite having typical pseudomorphic texture, containing primary Al-rich magnesiochromite (up to 18 and 16% of total concentration respectively). It is therefore justified that type and origin of ultrabasic parent rock affect metal mobility (at least in the case of Ni and Co) in serpentine soils. Furthermore, several soil characteristics (such as pH, total organic C, soil mineralogy) also play an important role in the mobility of Ni, Cr and Co. However, relationships between soil properties and metal availability are more pronounced for soils developed on proper serpentinites than for soils deriving from rocks that experienced less advanced serpentinization.

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1. Introduction

Ultrabasic rocks are scarce in the geological record as they represent part of the Earth mantle that was incorporated in the crust (Coleman, 1971). As such, they offer a unique insight into mantle composition and evolution (e.g., Puziewicz et al., 2015). The extended distance from the mantle to the crust changes the mineral composition of the rocks by various hydrothermal and metamorphic processes (e.g., Hyndman and Peacock, 2003). The final product of these processes is serpentinite. The ultrabasic rocks weather into soils with unusual chemical composition leading to unique plant communities worldwide (e.g., Harrison and Rajakaruna, 2011; Van der Ent et al., 2015).

Peridotite and serpentinite are characterized by similar chemical composition except for higher water content (up to 13%) in serpentinite compared to that in peridotite. Both these types of rocks have relatively low concentrations of silica (<45 wt.% of SiO₂) and high amounts of magnesia (> 35 wt.% of MgO) but are characterized by different mineral composition. The former is composed mostly of olivine, pyroxene with

minor spinel or Al-rich chromite, whereas the latter consists mostly of metamorphic phases such as serpentine group minerals with minor brucite, actinolite and magnetite and relics of primary olivine and pyroxene (Coleman, 1971; Mellini et al., 2005).

Soils derived from peridotite and serpentinite are commonly called serpentine soils due to the fact that similar vegetation cover occurs on both types of the rocks (Brooks, 1987). However, the soils have variable properties and are characterized by different morphology (Alexander and DuShey, 2011; Alexander, 2009). Soils derived from peridotites are generally more red than soils formed on serpentinites, which can be explained by differences in mineralogy between these rocks (Alexander, 2004). Major source of iron in serpentinites is magnetite, the phase, which is resistant to weathering, whereas in peridotites iron mostly occurs in olivine, which is more readily weathered (Alexander, 2004). Therefore, the iron is more easily released in soils developed from peridotites than in those derived from serpentinites, producing higher concentrations of iron oxides responsible for red color in the former soils (Alexander, 2004). Generally, serpentinites are more fractured, as a result of serpentinization and related deformation, than peridotites. Consequently, steeper slopes are observed on peridotites, whereas shallower soils and more pronounced landslides are reported for serpentinite terrains (Alexander and DuShey, 2011).

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Soils occurring in ultrabasic terrains are enriched in some metallic elements (e.g., Ni, Cr and Co; see for example [Venturelli et al., 1997](#); [Massoura et al., 2006](#); [Kierczak et al., 2007](#); [Quantin et al., 2008](#); [Alves et al., 2011](#); [Kelepertzis and Stathopoulou, 2013](#); [Bani et al., 2014](#)) compared to other soils forming under temperate climatic conditions. This specific composition causes metal toxicity which together with nutrient deficiency of serpentine soils make those terrains unfavorable for plant growing ([Proctor, 2003](#)). At the same time, these soils offer opportunities for the study of the mobility of the metals of geogenic origin ([Vithanage et al., 2014](#)). Of special interest is mobility of Ni and Cr and its relationships to mineral composition and physicochemical properties of serpentine soils. Generally, Ni is more mobile than Cr because the latter is bounded in phases more resistant to weathering such as Fe and Cr oxides (e.g., [Kierczak et al., 2007](#); [Quantin et al., 2008](#); [Cheng et al., 2011](#)). Furthermore, distribution and availability of Ni, Cr and Co are also controlled by soil mineralogy and topography. For example, [Bani et al. \(2014\)](#) show that higher Ni availability occurs in upslope soils enriched in iron oxides compared to soils found down-slope, where relative proportions of secondary smectites increase. Similarly, [Cheng et al. \(2011\)](#) noted that landscape position is the most important factor governing Ni and Cr distribution in soils. Moreover, Ni and Cr availability is correlated with some basic physicochemical soil properties such as Mg/Ca ratio, clay and organic carbon content ([Cheng et al., 2011](#); [Kelepertzis and Stathopoulou, 2013](#); [Bani et al., 2014](#)). On the other hand, [Alves et al. \(2011\)](#) did not observe any correlation between Ni bioavailability and organic carbon concentrations, but found that it may be controlled by the hydrous Mn oxides.

It is noteworthy that all of the above mentioned studies presenting the mobility of metals in soils formed on ultrabasic substrates do not take into account whether the parent rock is represented by igneous peridotite or metamorphic serpentinite. Generally, major components of peridotites (olivine, pyroxene) are less resistant to weathering than serpentine group minerals - principal components of serpentinites ([Alexander, 2004](#)). Furthermore, [Baumeister et al. \(2015\)](#) suggested that the degree of serpentinization, resulting in the extent to which primary minerals (e.g., pyroxene and olivine) remain within serpentinized peridotites, may play a controlling role in the formation of serpentine soils. It is therefore expected that the mobility of metallic elements should be affected by the type of the ultrabasic rock and should depend on the degree of alteration of the primary peridotite. The main objective of this paper is to determine whether and how the composition and texture of ultrabasic parent rocks affect distribution of selected metallic elements (Ni, Cr and Co) in soils developed from peridotites and serpentinites. We hypothesize that mobility of these metals should be higher in soils derived from peridotites than in soils formed on serpentinites. Furthermore, we investigate other factors that may also influence the mobility of metallic elements such as chemical and physicochemical properties of the soils. We used a set of mineralogical methods in order to identify the main Ni, Cr and Co bearing phases in ultrabasic rocks and several chemical extractions in order to determine potential mobility of studied metallic elements.

2. Geological and environmental settings of the study area

2.1. Diversity of parent ultrabasic rocks

Ultrabasic rocks and associated soils in Poland are located only in the Lower Silesia region (southwestern part of Poland; [Fig. 1a](#)). Serpentinite and/or partially serpentinized peridotite outcrops are found as small bodies (e.g., Żmijowiec, Popiel Hill) as well as parts of larger massifs of ultrabasic and basic rocks (e.g., Jordanów–Gogołów, Szklary Massifs; [Fig. 1](#)). From the geological point of view, Polish serpentinites and peridotites occur within the Sudetes, situated at the northeastern border of the Bohemian Massif, which represents the eastern part of the Variscan orogen in Europe ([Fig. 1b](#)). The Sudetes are divided into two morphological units by the Sudetic Boundary Fault: (1) a mountainous

southwestern part - the Sudetes Mountains and (2) a flat northeastern part - the Fore-Sudetic Block which is mostly covered by Cenozoic deposits. The whole area of the Sudetes forms a complex structural mosaic ([Fig. 1c](#)) and is composed of various types of geological units such as: (1) basement units which are composed of fragments of Cadomian crustal blocks, metamorphosed Paleozoic sediments, metaigneous complexes and Variscan granitoids and (2) post-Variscan cover consisting of Lower Carboniferous to Cenozoic sediments ([Kryza and Pin, 2010](#)). The largest massifs of ultrabasic rocks from the Polish part of the Sudetes area are located in the vicinity of the Góry Sowie block ([Fig. 1c](#)) which is one of the most extensive geological unit of the Sudetes. These massifs comprise: (1) Jordanów Gogołów Massif, (2) Szklary Massif, (3) Braszowice-Brzeźnica Massif and (4) Nowa Ruda Massif ([Fig. 1c](#)). These complexes of ultramafic and associated mafic rocks are interpreted as ophiolites and belong to the Central Sudetic ophiolites ([Dubinska and Gunia, 1997](#); [Kryza and Pin, 2010](#)).

Rocks and associated soils sampled for this study come from six sites located within relatively large massifs (Szklary Massif-site 1 and Jordanów–Gogołów Massif-sites 2–4) as well as from small occurrences of ultrabasites (Żmijowiec-site 5 and Popiel Hill-site 6).

The Szklary Massif outcrop is located in southern part of the Fore Sudetic Block (eastern border of the Góry Sowie Massif, [Fig. 1c](#)). This geological unit is composed of partially serpentinized peridotites which are cut by subordinate granitoids and lamprophyre veins. As a result of weathering under warm and humid climate of the Neogene, a thick (in some places up to 50 m) rust-colored lateritic crust was formed covering almost the entire area of the Massif. During the Pleistocene, the area of the Szklary Massif was covered by a continental ice sheet. Afterwards, as a result of a glacier regression, unweathered ultrabasic rocks were exposed. From the Quaternary, the Szklary Massif has been submitted to a temperate climate and, as a result of the weathering of ultrabasic rocks, a unique ecosystem has formed on soils enriched with Ni and Cr ([Kierczak et al., 2007](#)).

The Jordanów–Gogołów Massif is the largest body of ultramafic rocks adjacent to the northern border of the Góry Sowie massif ([Fig. 1c](#)). It has preserved complete ophiolitic sequence and comprises (1) serpentinized peridotites, (2) pyroxene- and amphibole-rich rocks - representing ultramafic cumulates, (3) metagabbros - mafic cumulates, (4) diabases and metabasalts - representing sheeted dykes and pillow lavas and (5) dark radiolaria-bearing metacherts - sedimentary cover ([Kryza and Pin, 2010](#); [Wojtulek et al., 2016](#)). The area occupied by ultramafic rocks within this massif is 20 km long and 3 km wide.

Ultrabasic site at Żmijowiec ([Fig. 1a, c](#)) is approximately 60 m high and is roughly elliptical in form crag (50 m long and 30 m high). The rocks from this site are classified as a serpentinite locally abundant in veinlets of talc and/or dolomite ([Smulikowski et al., 1977](#)). The serpentinite stock at Żmijowiec is interpreted as the Alpine-type association of ultrabasites emplaced into regionally metamorphosed surrounding rocks ([Smulikowski et al., 1977](#)).

Small occurrence of ultrabasic rocks located close to the Intra-Sudetic Fault (Popiel Hill, [Fig. 1c](#)) forms a pipe-shape body within amphibolites of the Karkonosze granite metamorphic cover ([Gunia et al., 1998](#)). Ultrabasic rocks from the Popiel Hill form a small body about 300 m thick and is found as an outcrop in an abandoned quarry. Ultramafic rocks from this site probably represent ultramafic cumulates formed during early stages of the fractional crystallization of the melt ([Gunia et al., 1998](#)).

2.2. Serpentine soils and climate of the study area

Serpentine soils from Poland (Fore-Sudetic Block) have been the subject of several studies ([Samecka-Cymerman and Kempers, 1994](#); [Weber, 1982](#)). After investigation of genesis and properties of 14 soil profiles developed from serpentinites and/or partially serpentinized peridotites, [Weber \(1982\)](#) noticed that investigated pedons principally derive from ultrabasic rocks; however, traces of non-ultramafic material

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