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QUANTIFICATION OF THE EFFECTS OF WEATHERING AND PEDOGENESIS IN MICA SCHIST REGOLITH MATERIAL (ZŁOTE MOUNTAINS, POLAND) USING MASS BALANCE ANALYSIS

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Abstract: Progression of weathering processes and pedogenesis result in changes in mineral and chemical composition of soils in comparison with non-wethered regolith. The optimal method of analyzing geochemical transformations caused by weathering, which occur together with pedogenic processes, is known as mass balance analysis. This method enables determining the absolute value of an element's enrichment or depletion in weathered soil material via the concentration of the element in parent material. The aim of the study is to analyze changes in the chemical composition of mica schists regolith on the example of the Złote Mountains and to estimate the soil-forming processes contribution to changes in the chemical composition of the analyzed soil-saprolite profiles. Obtained results indicate significant depletion of Mg, Ca and Na in soils due to leaching of alkaline substances. Another process leading to transformation of the chemical composition in soils of sandy texture is podzolization which causes depletion of Fe, Al and Mn in the upper part of regolith. On the other hand, biocycling is a process which can lead to an enrichment of the regolith with certain elements (P, K). Some changes of the chemical composition in analyzed profiles can be also attributed to the occurrence of geomorphic processes and aeolian supply.

Keywords: weathering, pedogenesis, mass balance analysis, mica schists, Złote Mountains

1. INTRODUCTION

Weathering and pedogenesis usually differentiate regolith into three components: soil, saprolite, and weathered rock (Stolt & Baker, 1994). The entire upper part of the lithosphere represents a matter of investigation for both geologists and pedologists. Saprolite, defined as isovolumetrically weathered bedrock that retains the structure of parent rock (Pavich, 1986), can be recognized as soil parent material. With proceeding pedogenesis, significant changes occur in the regolith. The most typical evidence of soil formation includes the accumulation of organic matter (humus), formation of soil structure, loosening of local mineral material (dilation), and shifts in chemical and mineral composition (Targulian & Krasilnikov, 2007). The soil is a qualitatively different environment characterized by geochemical transformation compared with weathered rock.

Chemical weathering in the upper part of the regolith (soil layer) involves significant changes in chemical composition connected with cation leaching. Weathering and subsequent cation leaching are reflected by increasing concentrations of elements such as Ca, Mg, Na, and K starting from the regolith surface to the saprolite (Courchesne et al., 2002; Fougère et al., 2015). On the contrary, some elements can be moved upwards the soil profile through biocycling (Gordon & Jackson, 2000; Lucas, 2001; Jobbágy & Jackson, 2004). Another factor that affects the change in chemical composition in surface horizons is atmospheric deposition connected with both human impact (Jersak et al., 1995; Jersak et al., 1997; Lichter, 1998; Nowack et al., 2001; Courchesne et al., 2002) and environmental processes (Derry & Chadwick, 2007).

Podzolization is a unique soil-forming process, as it leads to the decomposition of the primary and secondary minerals due to the influence of soil organic compounds (humus) (Lundstrőm et al., 2000). Therefore, it is both pedogenic as well as an example of weathering processes. Organic acids present in the soil solution affect the dissolution of minerals by complexing Fe and Al (Kodama et al., 1983; Lundström et al., 2000) and via a form of mobile organic-metal complexes transport them downwards the profile. As a result, the depleted E (eluvial) horizon in the upper part of the weathering profile is formed and occurs beneath the enriched in pedogenic oxides Bs (illuvial) horizon (Jersak et al., 1995; Courchesne et al., 2002).

The optimal method of analyzing geochemical transformations caused by weathering, which occur together with pedogenic processes, is known as mass balance analysis (MBA). The theoretical basis for this method was produced in the late 1980s by Brimhall and Dietrich (1987) and then developed and applied in several studies (e.g. Brimhall et al., 1992; Egli et al., 2001). MBA makes it possible to determine (isovolumetrically) the absolute value of an element's enrichment or depletion in weathered soil material via the concentration of the element in parent material. The enrichment-depletion values are quantified considering soil bulk density and with reference to the concentration of the given element, which occurs only in poorly weathered minerals (in practice – Ti or Zr). The use of these two elements in mass balance calculations is the biggest advantage of the MBA method in comparison with other methods of quantifying chemical composition.

MBA was applied first by its creators to determine weathering transformations in soils developed from ultramafic rocks in the state of Oregon as well as beach sands in California (Brimhall & Dietrich, 1987). In later years, Jersak et al., (1995) used MBA to show extensive mineral weathering concurrent with organic matter accumulation in well-developed Podzols derived from Quaternary tills and glacial outwash. This method was also used to quantify (1) losses of carbonates from loess weathering profiles in the Alps' piedmont (Egli & Fitze, 2001) and (2) progression of weathering processes and change in mineral composition in soils developed from carbonate rocks (Egli et al., 2008). In Poland, this method was applied in studies on the formation of soil properties and when determining the soil chronosequence in the zone above the upper timberline in the Tatra Mountains (Drewnik, 2008).

Most of the studies concerning elements' mass balance in soils have focused on regolith of sedimentary origin (glacial, periglacial); only a few focus on soils developed from crystalline rocks.

The aim of this study was to analyze changes in the chemical composition of regolith crystalline rocks occurring in the Złote Mountains in Poland using mass balance analysis as well as the answer to the following key question: What is the contribution of soil-forming processes to changes in the chemical composition of the analyzed soils?

2. MATERIALS AND METHODS

2.1. Study area

The studied part of the Złote Mountains belongs to a variegated Stronie series built of metamorphic rocks formed between the end of the Proterozoic and the Cambrian – a part of the wide Lądek-Śnieżnik Metamorphic Unit (Don et al., 2003). The regional diversity of the Stronie formation is the result of lithological differences in sedimentary-volcanic protolith genesis as well as a complex tectonic history (Smulikowski, 1979; Don et al., 2003). Profiles selected for the purpose of this research were located on the southern slopes of Mount Czernica, built mainly of mica schists. Their mineralogical and petrographic characteristics are given by Smulikowski (1979) and indicate very distinct foliation, abundance of micas, and relatively low content of quartz/silica and plagioclases. The main cause of variability in the chemical composition of mica schists is related to variable proportions of main rock-forming minerals in part related to the feldspathization process (Milewska, 1958 after Don et al., 2003). Kabała (2005) observed a high concentration of iron bound to non-weathered silicates as well as a high content of alkaline components in soils developed from mica schist regolith in the nearby Śnieżnik Massif. The chemical composition of this soil results in a relatively weak expression of the podzolization process in comparison with soils developed from different parent material (gneiss) in the study area (Kabała, 2005).

Climate conditions in the Złote Mountains are typical for Central European subdued mountains with a significant effect of elevation and topography on temperature and rainfall spatial differentiation. Temperature statistics were estimated on the basis of records obtained from Lądek Zdrój (460 m a.s.l., approx. 12 km from the study area; Sobik, 2005), taking into account the decrease in temperature with elevation. Therefore, the mean annual temperature is approximately 3.5 to 4.5ºC, with mean temperature for July at around 13 to 13.5ºC and –5°C for January. Mean annual precipitation in nearby Bielice (690 m a. s. l., approx. 2 km from the study area; Sobik, 2005) reaches 944 mm with the highest rainfall in spring (246 mm) and summer (333 mm).

Vegetation in the Złote Mountains is similar to that in other mountain ranges in the Sudetes and is dominated by spruce (Picea abies) monoculture forests, which were introduced at the end of the 18th century in place of potentially natural Luzulo nemorosae-Fagetum with a significant admixture of fir (Bugajski & Nowiński, 1983; Zimny, 1996). In recent years, potentially natural forests remain scattered in small areas across the Sudetes (Matuszkiewicz, 2008).

The presented research is based on an investigation of two soil profiles located on the southern slopes of Mount Czernica. Profile 1 was situated on a vast summit flat, while Profile 2 on the upper part of the slope (Fig. 1). Vegetation at both investigated sites is semi-natural Fagus sylvatica forest (Table 1). This prevents any disruptive effects due to coniferous forest introduced by man (possible enhancement of weathering processes).

2.2. Field and laboratory methods

Profiles were studied in pits dug to a depth allowing saprolite exposure – 0.7 m and 0.95 m for Profiles 1 and 2, respectively. Samples from distinguished soil horizons were collected from pits both in undisturbed shape, using a core with a volume of 95 cm^3 – to determine bulk density – and in disturbed shape for other types of laboratory analysis. The volume of coarse fragments (stones) was estimated directly in pits using a standard template included in Guidelines for Soil Description (Jahn et al., 2006). The volume of fine roots was also obtained in the field by estimating the number of roots in an area of 100 cm^2 on the profile's face.

Laboratory analyses were carried out for samples of soil crushed using a soft tool and sieved through 2 mm mesh (fine soil). Texture was determined using the combined hydrometer and sieving method (Gee & Bauder, 1986; van Reeuvijk, 2002) without removal of organic matter, carbonates, and secondary oxides. This was done intentionally to avoid any changes resulting from the dissolution of organic-mineral compounds present in the soil. Soil pH was measured potentiometrically in deionized water and 0.01 M $CaCl_2$ with a soil:solution ratio of 1:1 (Thomas, 1996). The concentration of total carbon (TC) and total nitrogen (TN) was determined using gas chromatography as well as a micro-analyzer vario MICRO cube. The concentration of pedogenic ("free") Fe was determined in a citrate-bicarbonate-dithionite extract (van Reeuwijk, 2002) using CP-MS. Total chemical composition of mineral material was obtained using ICP-ES; LOI was determined at 400°C over 16 h (Nelson & Sommers, 1996).

2.3. Mass balance calculations

In order to determine and quantify changes in chemical composition in analyzed soil profiles, the mass balance model was introduced by Brimhall and Dietrich (1987), and then developed further by Chadwick et al., (1990). Brimhall et al., (1992) applied the model in their calculations. Calculation of the mass balance of elements in each studied profile is based on strain index values (ε), which inform about the net volume change in the analyzed weathered material in relation to the volume of the original non-weathered material; thus, about material dilation or compaction.

The calculation of strain was performed by taking into account an element present in minerals very resistant to weathering and therefore considered to be immobilized in the soil profile; in this case – zirconium (Zr).

The strain value is calculated using the equation below (Brimhall & Dietrich, 1987):

$$\varepsilon = \frac{\rho_p C_{i,p}}{\rho_w C_{i,w}} - 1$$

where ρ_p is the bulk density of the parent material, ρ_w – bulk density of weathered material, $C_{i,p}$ – concentration of immobile element (Zr) in the parent material, and $C_{i,w}$ – concentration of this immobile element in weathered material.

If the strain value is positive, it means that weathered material has been dilated in comparison with parent material. If the value is zero, then no volume change has occurred, and if the value is negative, weathered material has been compacted in relation to original non-weathered material.

The final stage of the mass balance calculation is determining the τ value for each analyzed element in relation to the parent material (Brimhall & Dietrich, 1987):

$$\tau = \frac{\rho_w C_{j,w}}{\rho_p C_{j,p}}(\varepsilon + 1) - 1$$

$C_{j,w}$ and $C_{j,p}$ are concentrations of the analyzed elements in weathered and parent material, respectively.

The deepest, exposed part of the studied profile was selected as a reference point in mass balance calculations (part which has no pedogenic structure = saprolite): 55–70 cm in Profile 1, and 80–95 cm in Profile 2 (soil horizons: C).

3. RESULTS

3.1. Morphology, physical and chemical properties

Both studied soils have the same horizonation or internal structure of the soil profile. Litter at different stages of decomposition is present (O-horizon) on the surface of the mineral part of the soil (regolith).

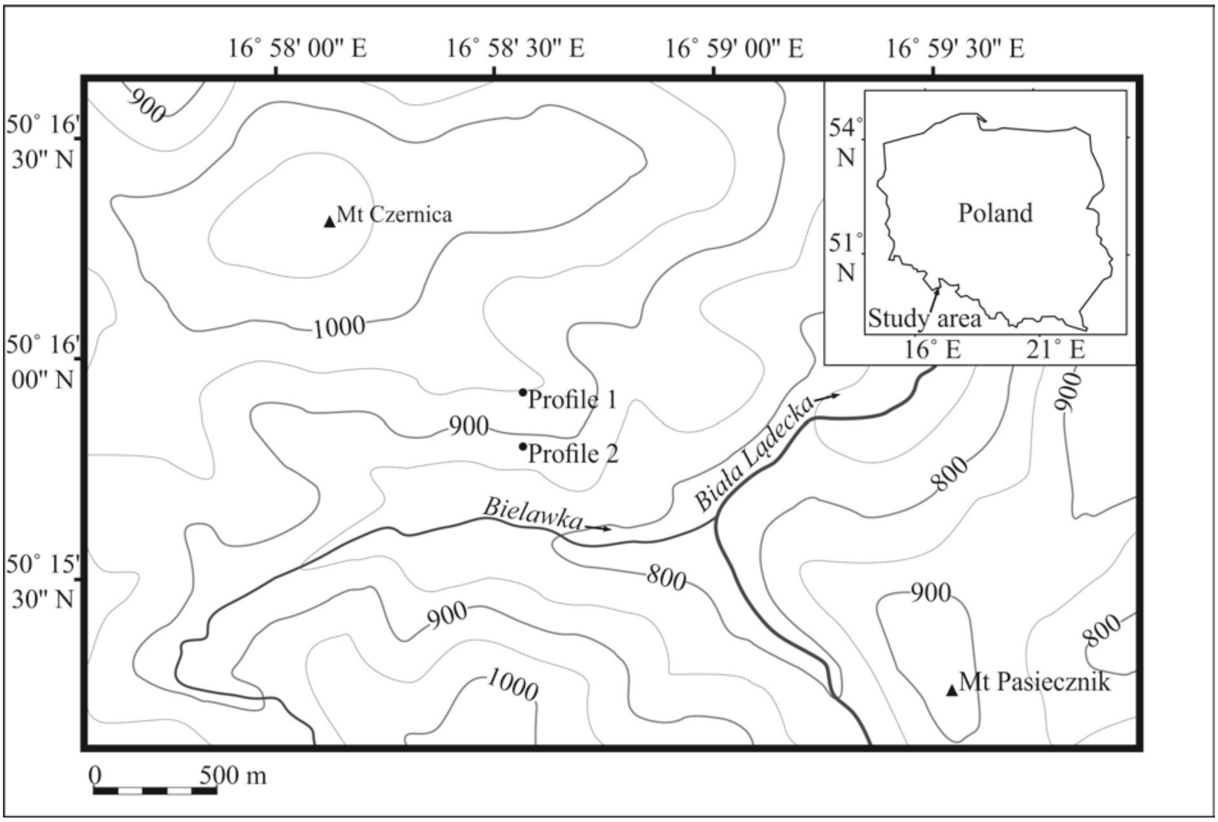

Figure 1. Location of the study area and the investigated profiles.

Table 1. Investigated profiles

Topography	Coordinates WGS 84	Parent material	Elevation	Slope angle	Slope aspect	Vegetation
Profile 1						
Summit flat	50° 15' 55" N; 16° 58' 37" E	mica schists	945 m a. s. l.	5°	S	*Fagus sylvatica*, European beech
Profile 2						
Middle slope	50° 15' 48" N; 16° 58' 35" E	mica schists	880 m a. s. l.	15°	S	*Fagus sylvatica*, European beech

The uppermost part of the mineral soil begins with a grey-colored horizon with mixed characteristics (AE): accumulation of humus (A-horizon) and the horizon of eluviation (E-horizon). Reddish-black-colored illuvial horizons occur deeper and feature a black and rust color in their upper part (Bhs-horizon) and a rust color in the lower part (Bs-horizon). The illuvial horizon B gradually transforms (transition horizon BC) into parent rock material (C-horizon = saprolite). An abundance of fine roots was noted in the analyzed soils: 50–200 fine roots per 100 cm^2 to a depth of around 40 cm and to a depth of 60 cm in Profile 1 and Profile 2, respectively. Single roots were found below these depths in both soils.

The content of stones in the soil mass in both soils was significant. Profile 1 contained 30% to 40% coarse fragments within its uppermost 15 cm of the mineral part of the soil (below organic O-horizons) and 50% to 80% below this depth (Table 2). In Profile 2 near the surface, coarse fragment content was around 50%; in the middle part of the analyzed profile, the thickness decreased to 10% to 30%, and in the saprolite, it again increased to 50% to 60%. The texture of both soils is sandy loam throughout the analyzed thickness (Table 2). In the C horizon of Profile 1, the soil texture turns towards loam. This soil contains also about 10% more silt in its middle part in comparison with Profile 2. Bulk density in the organic O-horizons reaches 0.13 and 0.23 $g\cdot cm^{-3}$ (Profiles 1 and 2, respectively) and gradually increases with depth to reach a value of 0.71 $g\cdot cm^{-3}$ in the saprolite (soil horizon: C) (Table 2).

The content of organic matter in both analyzed soils was determined to be high. With the exception of organic O-horizons (399–517$g\cdot kg^{-1}$ TC), the content of TC in the uppermost mineral part of the soil (AE1-horizon) was 124.2$g\cdot kg^{-1}$ and 193.7$g\cdot kg^{-1}$ in Profiles 1 and 2, respectively. As the depth of the soil increased, the content of organic matter became smaller, even in the saprolites, the content of TC was 17.3g·kg^{-1} and 28.6g·kg^{-1} TC in Profiles 1 and 2, respectively. The C/N ratio was in the 18-24 range in the organic material in O-horizons, while in the mineral part of the analyzed profiles, it was in the 13–17 range (Table 2). The pH of both profiles was either acidic or very acidic. The pH measured in H2O was 3.3–4.3 in the organic O-horizons of both soils, 3.2–3.4 in AE horizons, 4.0–4.6 in Bhs and Bs horizons, and 4.6–4.7 in C horizons (pH was lower in each case in a $CaCl_2$ solution) (Table 2).

Both soils have properties and morphology typical of soils classified as Spodosols and Podzols according to the USDA Soil Taxonomy (Soil Survey Staff, 2014) as well as World Reference Base for Soil Resources (IUSS Working Group WRB, 2014).

3.2. Chemical composition

The chemical composition of the analyzed soils was dominated by SiO_2 (40% to 65%), Al_2O_3 (8% to 15%), and Fe_2O_3 (2% to 9%) (Table 3). The share of MgO, CaO, Na_2O, K_2O, and TiO_2 did not exceed 3%; the content of P_2O_5 and MnO was marginal (<0.3%) (Table 3).

The vertical distribution of SiO_2 throughout each profile varied, with the highest SiO_2 content in C horizons (Table 3). Al_2O_3 and Fe_2O_3 show similar vertical differentiation: a decrease in horizons AE followed by a significant increase – reaching maximum content in horizons Bhs and Bs of the analyzed soils. Maximum content of Al_2O_3 occurred deeper than the highest Fe_2O_3 content.

The content of MgO, CaO, and Na_2O increased with increasing depth; however, in Profile 2, relatively high values of CaO and Na_2O were determined in the AE horizons. In the middle part of Profile 2, a decrease in these components was noted and again an increase in the BC soil horizon.

The upper parts of both soils feature a relatively higher share of K_2O in comparison with the horizons beneath. The maximum concentration of K_2O occurred in saprolites. P_2O_5 and MnO content in Profile 1 shows a relative increase with depth to the horizon Bhs2 and a decrease in horizon C. In Profile 2, concentrations of P_2O_5 and MnO are comparable throughout the analyzed thickness. A comparison of the chemical composition of soils between Profiles 1 and 2 reveals a few significant differences (Table 3).

Table 2. Morphology, physical and chemical properties of investigated profiles.

Depth [cm]	Soil horizon	Fine roots	Coarse fragment content [% vol.]	Fine fractions content [% weigh]			Bulk density [g·cm^{-3}]	Total carbon content [g·kg^{-1}]	C:N ratio	pH [H_2O]	pH [$CaCl_2$]
				2–0,05 mm	0,05–0,002 mm	<0,002 mm					
Profile 1											
4–3	Oi	n.d.	0	n.d.	n.d.	n.d.	0.13	405.3	19	4.0	3.6
3–1	Oe	n.d.	0	n.d.	n.d.	n.d.		434.1	18	3.4	2.9
1–0	Oa	n.d.	0	n.d.	n.d.	n.d.		399.7	18	3.3	2.9
0–3	AE1	+++	30	n.d.	n.d.	n.d.	0.35	124.2	14	3.2	3.0
3–6	AE2	+++	40	n.d.	n.d.	n.d.	0.29	94.7	15	3.5	3.2
6–11	Bhs1	+++	40	65	26	9	0.27	91.7	14	4.0	3.6
11–36	Bhs2	+++	50	53	36	11	0.41	60.2	13	4.6	4.3
36–55	BC	few	50	55	34	11	0.45	50.4	13	4.6	4.3
55–70	C	few	80	47	43	10	0.71	17.3	16	4.6	4.4
Profile 2											
4–3	Oi	n.d.	0	n.d.	n.d.	n.d.	0.23	516.9	24	4.1	3.8
3–0	Oe	n.d.	0	n.d.	n.d.	n.d.		438.8	21	4.3	3.5
0–4	AE1	+++	50	n.d.	n.d.	n.d.	0.39	193.7	13	3.4	3.0
4–11	AE2	+++	10	n.d.	n.d.	n.d.		118.8	17	3.8	3.3
11–14	Bhs1	++	10	71	17	12		104.8	15	4.1	3.6
14–36	Bhs2	++	30	69	19	12	0.36	108.5	14	4.5	3.9
36–60	Bs	++	30	66	23	11	0.41	70.7	17	4.5	4.1
60–80	BC	few	50	57	34	9	0.71	25.8	15	4.7	4.3
80–95	C	few	60	60	30	10	0.71	28.6	16	4.7	4.3
80–95	C	few	60	60	30	10	0.71	28.6	16	4.7	4.3

n.d. – not determined; +++ – 50–200 fine roots per 100 cm^2; ++ – 20–50 fine roots per 100 cm^2;
+ – less than 20 fine roots per 100 cm^2

Table 3. Chemical composition.

Depth [cm]	Soil horizon	SiO_2 [%]	Al_2O_3 [%]	Fe_2O_3 [%]	MgO [%]	CaO [%]	Na_2O [%]	K_2O [%]	TiO_2 [%]	P_2O_5 [%]	MnO [%]	Zr [%]	LOI [%]
Profile 1													
0–3	AE1	60.82	9.24	1.71	0.36	0.52	1.07	2.30	0.63	0.13	0.02	0.03	23.1
3–6	AE2	61.52	10.33	3.44	0.50	0.52	1.07	2.42	0.77	0.15	0.05	0.03	19.1
6–11	Bhs1	51.46	10.49	6.71	0.60	0.51	0.98	2.10	0.72	0.20	0.08	0.02	26.0
11–36	Bhs2	56.05	13.54	4.98	0.75	0.61	1.23	2.37	0.75	0.24	0.16	0.02	19.2
36–55	BC	56.14	14.01	5.15	1.15	0.69	1.26	2.27	0.70	0.27	0.11	0.02	18.1
55–70	C	64.67	13.83	5.15	1.77	0.98	1.62	2.57	0.80	0.15	0.07	0.04	8.2
Profile 2													
0–4	AE1	44.52	8.4	3.69	1.36	1.89	1.23	1.16	0.85	0.14	0.05	0.02	36.5
4–11	AE2	54.19	10.43	5.58	1.68	2.24	1.56	1.48	1.03	0.09	0.07	0.03	21.5
11–14	Bhs1	43.31	10.97	9.14	1.64	1.87	1.42	1.17	0.92	0.16	0.07	0.02	29.2
14–36	Bhs2	40.46	12.64	7.93	1.63	1.69	1.25	1.20	0.84	0.16	0.08	0.02	32.0
36–60	Bs	45.95	15.27	6.45	1.87	1.41	1.40	1.50	0.77	0.14	0.08	0.02	25.0
60–80	BC	57.37	15.23	6.33	2.48	1.94	1.95	1.85	0.85	0.12	0.08	0.03	11.6
80–95	C	57.32	14.66	6.20	2.53	1.97	1.88	1.89	0.87	0.12	0.08	0.03	12.3

In Profile 1, the content of SiO_2 is 5–15% higher compared with corresponding horizons in Profile 2, and the concentration of K_2O is almost double that in Profile 2. Moreover, the MgO and CaO content show a significantly lower share throughout Profile 1 in comparison with Profile 2. The Fe_2O_3 content in Profile 1 is also slightly lower than that in Profile 2.

Table 4. Content of CBD-extracted iron, weathering ratio (Fe_d/Fe_t) values and Ti/Zr ratio values.

Depth [cm]	Soil horizon	Fe_d [%]	Fe_d/Fe_t	Ti/Zr
Profile 1				
0–3	AE1	0.50	0.41	14.5
3–6	AE2	1.12	0.46	17.1
6–11	Bhs1	2.69	0.57	18.8
11–36	Bhs2	1.71	0.49	18.7
36–55	BC	1.42	0.39	17.5
55–70	C	0.49	0.14	13.7
Profile 2				
0–4	AE1	0.66	0.26	25.5
4–11	AE2	1.38	0.35	22.9
11–14	Bhs1	2.97	0.46	29.0
14–36	Bhs2	2.32	0.42	25.2
36–60	Bs	1.40	0.31	23.1
60–80	BC	0.71	0.16	19.6
80–95	C	0.67	0.15	18.6

The content of CBD-extracted iron (Fed) freed from mineral structures as a result of weathering is similarly low in both analyzed soils and reaches a maximum in Bhs horizons (Tab. 4).

In the uppermost part of the soil, the share of Fed in total Fe is 26% to 41%, reaching maximum values of 46% and 57% at a depth of around 15 cm, and below this depth decreases with depth to reach minimum values of 14% and 15% in saprolites. Slightly higher Fed/Fet values, particularly values in near-surface horizons, were calculated for Profile 1.

The vertical distribution of the Ti/Zr ratio (Table 4) does not exhibit significant differences between the analyzed profiles as well as throughout each studied profile.

3.3. Element mass balance

MBA results show significant changes in the chemical composition of the analyzed soils based on strain index values (Table 5). Strain values (εZr,w) are positive for the entire analyzed thickness and vary from 1.3 and 1.4 in the soil-saprolite transition zone to 1.7 and 2.9 in the Bhs and Bs horizons.

Higher values were determined for Profile 1, particularly in the middle part, where strain values are double those determined for Profile 2.

The results of mass balance (τ) for Si indicate enrichment with this element throughout both analyzed soils (Table 5). In Profile 1, enrichment with Si is more significant, up to 30% (e.g. τ values of 0.27–0.28) in some parts, whereas in Profile 2, the enrichment level varies from 0.01 to 0.11. The mass balance of Al and Fe in both soils shows pronounced depletion of uppermost horizons, up to 22% for Al (τ = –0.22 in Profile 2, horizon AE2) and 55% (τ = –0.55 in Profile 1, horizon AE1) for Fe. In the middle part of the soil, a significant enrichment occurs in relation to the concentration of these elements in the saprolite, exceeding 40% for Al (τ = 0.45 in Profile 1, horizon BC) and 115% for Fe (τ = 1.16 in Profile 2, horizon Bhs1). The loss of Al is relatively smaller in Profile 1 than in Profile 2. On the other hand, the upper part of Profile 1 contains three times less Fe compared with Profile 2.

Table 5. Strain and mass balance values.

Depth [cm]	Soil horizon	ε(Zr,w)	Element mass balance (τ)								
			τ(Si)	τ(Al)	τ(Fe)	τ(Mg)	τ(Ca)	τ(Na)	τ(K)	τ(P)	τ(Mn)
Profile 1											
0–3	AE1	1.7	0.28	-0.09	-0.55	-0.72	-0.28	-0.10	0.22	0.18	-0.61
3–6	AE2	2.2	0.24	-0.03	-0.13	-0.63	-0.31	-0.14	0.23	0.30	-0.07
6–11	Bhs1	2.9	0.21	0.15	0.98	-0.48	-0.21	-0.08	0.24	1.03	0.74
11–36	Bhs2	1.6	0.27	0.43	0.42	-0.38	-0.09	0.11	0.35	1.34	2.35
36–55	BC	1.3	0.25	0.45	0.43	-0.07	0.01	0.12	0.27	1.58	1.25
55–70	C	-	-	-	-	-	-	-	-	-	-
Profile 2											
0–4	AE1	1.5	0.09	-0.19	-0.16	-0.24	0.35	-0.08	-0.14	0.64	-0.12
4–11	AE2	1.0	0.03	-0.22	-0.02	-0.27	0,24	-0.09	-0.14	-0.18	-0.04
11–14	Bhs1	1.7	0.11	0.10	1.16	-0.05	0.39	0.11	-0.09	0.95	0.28
14–36	Bhs2	1.9	0.01	0.24	0.84	-0.07	0.23	-0.05	-0.09	0.91	0.44
36–60	Bs	1.4	0.11	0.44	0.44	0.02	-0.01	0.03	0.10	0.62	0.39
60–80	BC	0.1	0.09	0.13	0.11	0.07	0.07	0.13	0.07	0.09	0.09
80–95	C	-	-	-	-	-	-	-	-	-	-

Considerable depletion of Mg in the upper part of both analyzed soils was observed. However, in Profile 1, losses of Mg exceeded 65% in its uppermost horizons, while in Profile 2, the maximum negative τ value was –0.27. Profile 1 is fully depleted with respect to Mg in relation to the original concentration in the parent material, whereas in horizons Bs and BC of Profile 2, there occurs a zone with some Mg enrichment. Similar results were obtained for the Ca mass balance in Profile 1. Losses of 20% to 30% were noted throughout the profile to a depth of 40 cm. The results for Profile 2 are entirely different, showing significant enrichment of the soil's upper 40 cm up to 39%.

The vertical distribution of τ values for K concentrations indicates enrichment with this element throughout the entire Profile 1, with maxima of 0.27 and 0.35 occurring below a depth of 15 cm. Profile 2 shows opposite results with K losses around 10% in the uppermost 40 cm of the soil and a slight increase occurring below this depth

Both profiles demonstrate small losses of Na at approximately 10% in AE horizons (in Profile 1 as well as the Bhs1 horizon) and below correspondingly gains with maximum values of 11% to 13% occurring in the lowest analyzed horizons.

Another element showing a distinct increase in concentration, according to MBA, is P. The entire thickness of Profile 1 is enriched with this element with τ values varying between 0.18 in the AE1 horizon and 1.58 in the horizon BC. Profile 2 shows similar increases in P content in the soil, with a maximum value of 0.95 in the Bhs1 horizon, except for the horizon AE2, which shows a negative τ value.

The vertical distribution of Mn τ values is similar to that obtained for Al, Fe, and Na, showing depletion in AE horizons and enrichment in the middle and lower parts of the studied soils. The depletion of Mn reaches 61% and 12% in the AE horizons of Profiles 1 and 2, respectively, while enrichment varies between 74% and 125% in Profile 1 and 28% and 44% in Profile 2. However, the very small quantity of Mn and P should be taken into consideration while analyzing the results of the mass balance for these two elements.

4. DISCUSSION

The studied soils developed from similar parent material, which is shown by the Ti/Zr ratio, which can be considered an indicator of mineral material homogeneity. A high content of coarse fragments is a typical property of relatively young mountain soils derived from crystalline rocks (see Skiba, 1977; Drewnik, 2008) and it affects other soil physical properties. One of its consequences is very low bulk density of fine soil determined by a high coarse fragment content – stones increase the porosity of the soil in the course of its freezing point (Van Vliet Lanoë, 2010). Low bulk density is also connected with a high amount of organic matter accumulated in soil profiles to a significant depth as well as with an abundance of roots throughout the soil (Kubica et al., 2010).

High strain values obtained in this study throughout the studied soil profiles reflect the impact of the above factors and are similar to results obtained by Jersak et al., (1995) and Drewnik (2008). A comparison of the obtained strain results with the dependence of soil age on strain values listed by Brimhall et al., (1992) indicates a relatively young age of the studied soils (Egli et al., 2014). Low values of the Fed/Fet ratio, considered to be an indicator of the weathering rate (Degórski, 2005), also confirm the hypothesis of a primary stage of soil evolution in the Złote Mountains. However, relative differences in strain values as well as in the Fed/Fet ratio between the studied profiles indicate slightly more advanced pedogenesis in Profile 1 than in Profile 2. This may be the result of more intensive vertical water percolation in the profile located on a summit flat in comparison with the profile located on a slope where the effect of lateral water movement gains some significance (Sommer & Schlichting, 1997; Sommer et al., 2001). Despite the fact that the described soils are relatively young, they have a quite well-developed morphology and properties that are no longer classified as initial or poorly developed.

The studied soil profiles feature typical properties of mountain soils developed from crystalline rock regolith in a humid cold climate (Kabała, 2005; Lundström et al., 2000; Skiba, 1977). The arrangement of soil-forming factors generates two main processes considered to be typical soil-forming processes in the investigated area: accumulation of organic matter and podzolization. The presence of a few centimeters of organic horizon on the surface (litter) and a high content of humus in the soil are the results of a cold humid climate. According to USDA Soil Taxonomy (Soil Survey Staff, 2014), the soil temperature regime in the studied area is “cryic” and the soil moisture regime is “perudic”. Accumulated organic matter affects the mineral part of the soil as a source of soluble humic acids, which enables leaching of base cations and the development of the podzolization process (Lundström et al., 2000). The low values of soil solution pH are primarily connected with the significant influence of acidic organic matter throughout the analyzed thickness as well as with a small share of alkaline components (Lundström et al., 2000).

The most significant changes in the chemical composition, and at the same time, the largest net losses in the analyzed soils are linked with the leaching of basic cations. Despite a small share of Mg, Ca, and Na, the depletion level of these elements is relatively substantial, particularly in the near-surface zone. Results obtained for soils developed from different types of parent material (igneous and metamorphic rocks as well as glacial sediments) in different geographic regions show similar levels of depletion of these elements (Jersak et al., 1995; Olsson & Melkerud, 2000; Schaller et al., 2010; Fougère et al., 2015). The largest losses usually apply to Mg and reach 50% to 85% in the uppermost parts of profiles. The next largest losses apply to Ca, with maximum losses at 50% to 70%. The depletion of Na usually reaches 40% to 50%. Results obtained by Courchesne et al., (2002) in soils from Southern Québec (Canada) indicate a slightly higher mean annual loss of Ca, which varies from 1.30 to 7.05kg$\cdot$ha$^{-1}\cdot$year^{-1} compared with Mg (0.91–3.33kg$\cdot$ha$^{-1}\cdot$year^{-1}). However, the relative mobility of Mg in the analyzed profiles is higher than that of Ca. Enrichment with Ca observed in Profile 2 is most likely the outcome of subsurface lateral solution translocation, which may affect the chemical composition of regolith material at lower positions on the slope (Sommer & Schlichting, 1997).

All of the discussed studies considering the distribution of alkaline substances in soils (Jersak et al., 1995; Olsson & Melkerud, 2000; Courchesne et al., 2002; Schaller et al., 2010; Fougère et al., 2015) indicate more or less significant losses of K in their upper parts due to ongoing weathering and leaching. Similar results showing depletion of K in the uppermost 40 cm of the soil were obtained for Profile 2. However, the K mass balance for Profile 1 exhibits exactly the opposite process, which may be linked with biocycling leading to a redistribution of cations in the soil profile (Jobbágy & Jackson, 2004). Cations are often used by plants; combining them in the aboveground biomass and returning them to the soil surface through litterfall or decay leads to enrichment of the uppermost soil horizons (Lucas, 2001; Jobbágy & Jackson, 2001; Jobbágy & Jackson, 2004). K content can vary from 5 to even 80mg$\cdot$g^{-1} in plant dry matter (Callot et al., 1982; Epstein, 1994). Positive results associated with the P mass balance in the analyzed profiles can be also attributed to the biomass turnover process and accumulation of organic matter (Jobbágy & Jackson, 2001).

The enrichment with Si determined in the analyzed profiles may be also connected with the source of biocycling. Annual turnover of Si in temperate climates in relation to the diversity of vegetation and soil type varies from 3 to 7kg$\cdot$ha$^{-1}\cdot$year^{-1} in coniferous forests to 30 to 45kg$\cdot$ha$^{-1}\cdot$year^{-1} in deciduous forests (Bartoli, 1986; Bartoli & Souchier, 1978). Moreover, Watteau et al., (2001) observed significant amounts of Si stored within the cells of beech leaves and roots in the form of polyphenolic substance coatings and associations with the pecto-cellulosic matrix. On the other hand, studies on the Si mass balance indicate a rather slight depletion of this element in the upper part of the soil profile, as opposed to its increase (Jersak et al., 1995; Olsson & Melkerud, 2000; Courchesne et al., 2002).

Atmospheric deposition can be considered yet another factor, which could explain the positive results associated with the Si and K mass balance in the analyzed soils. In urban and agricultural areas, Si total atmospheric deposition values reaching averages of 3 and 6 kg$\cdot$ha$^{-1}\cdot$year^{-1} (Johnson & Eisenreich, 1979; Anderson & Downing, 2006); however, Bolan et al., (2011) indicate that little Si is usually accrued in the soil via atmospheric deposition. More significant Si deposition may have occurred under Pleistocene periglacial conditions (Kleber, 1997) on some slopes free of vegetation due to windblow transport of Si-rich silt. Relatively more flat/planar slopes may have been areas where significant silt deposition had taken place. In the middle part of the analyzed Profile 1, the relatively higher amount of the silt fraction was determined in comparison with Profile 2, which was located on a steeper slope. That difference could be considered to be one piece of evidence of past silt deposition on the analyzed slope (see Kleber, 1997). K atmospheric deposition values noted in different climate conditions are relatively high (Ferm et al., 2000; Moreno Marcos & Gallardo Lancho, 2002) and such high values can also be responsible for K enrichment in Profile 1 (assuming ongoing biocycling).

Podzolization is a factor that leads to significant depletion of Al, Fe, and Mn in the uppermost part of the soil and a large increase in the concentration of these elements in its middle parts due to the precipitation of secondary oxides. Results obtained in Poland’s Złote Mountains show similar differentiation within soil profiles in relation to mass balance studies conducted on glacial sediments (Jersak et al., 1995; Olsson & Melkerud, 2000; Courchesne et al., 2002), although the enrichment values in our study are significantly higher. The main reason for this is higher absolute concentrations of Al and Fe in comparison with sediments of glacial origin. Moreover, the analyzed mica schist material, as illustrated by the obtained Fed/ Fet ratio, is relatively poorly weathered; hence, the major part of mineral material remains in non-weathered form yielding high Fe content. Significant differences in the Mn mass balance in the analyzed profiles can be also attributed to the process of podzolization, as Mn is strongly mobile in acidic environments (Kabata-Pendias, 2000) and often precipitates in the form of secondary oxides.

5. CONCLUSIONS

The properties of soils occurring in the Złote Mountains are typical of mountain areas, with a significant influence of the cold and humid climate. Both profile morphology and the properties of soils show that the soils are well-developed. However, from the point of view of weathering, these soils are relatively young, as they remain characterized by positive strain values (volume expansion).

The degree of depletion of alkaline elements and their distribution within each given soil profile indicate that soil-forming processes play an essential role in weathering processes in the regolith. Occurrence of podzolization process can also lead to significant changes in chemical composition, particularly in the case of elements such as Fe, Al and Mn which form very mobile organic-metal complexes in the acid environment. In the case of certain elements (P, K), biocycling leads to an enrichment of a weathering profile with these elements; in some cases, even to a full enrichment of regolith. Some changes in the chemical composition of the studied soils can be attributed to local geomorphic processes. The enrichment of the regolith in Si in the soil of an expansive summit flat is most likely a result of aeolian material supply. On the other hand, Ca-enrichment in the soil of the steep slope is associated with element translocation down the slope.

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