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ANDESITE WEATHERING AND SOIL FORMATION IN A MODERATELY HUMID CLIMATE: A CASE STUDY FROM THE WESTERN CARPATHIANS (SOUTHERN POLAND)

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Abstract: The main aim of this study was to describe andesite weathering and soil formation in a moderately humid climate based on the physical, chemical, and micromorphologic properties of soil profiles from the Western Carpathians in southern Poland. Andesite weathering and soil formation in a moderately humid climate are reflected by significant depletion of SiO_2, Al_2O_3, CaO, and Na_2O from soils in relation to unweathered andesite bedrock. The chemical index of alteration and weathering (CIA and CIW) and plagioclase index of alteration (PIA) as well as weathering index of Parker (WIP) all indicate that soil material obtained from all the studied profiles (except the Jarmuta profile, which is enriched in carbonate by meteoric water during the Holocene) is clearly more weathered in comparison with andesitic bedrock. However, these chemical indexes do not show clear differences in weathering degree of soil material between different soil horizons, which is most likely related to excessively thin soil profiles and/or the occurrence of lithologic discontinuities in some of them. Micromorphologic observations indicate that in the process of weathering many fragments of andesite undergo cracking and iron in the phenocrysts of hornblende and augite undergoes oxidation. The crystals of hornblende exhibit very often irregular linear alteration along lines of cleavage. Additionally, many fragments of andesite and coarser mineral grains are characterized by the presence of weathering rims, which are composed mainly of iron hydroxides, clay minerals together with iron hydroxides, and sometimes also organic matter.

Keywords: andesite, geochemistry, leaching, micromorphology, soil formation, weathering

1. INTRODUCTION

Weathering is one of the most important and common processes operating on the Earth's surface due to the interaction of the lithosphere, atmosphere, and biosphere. This vital process is responsible for the decomposition of rocks and minerals as well as soil formation. Weathering also affects the transformation and neoformation of minerals as well as release of elements essential for plant nutrition (Wilson, 2004). Secondary minerals formed during weathering such as clay minerals and iron and aluminum oxides can fix and neutralize many pollutants, making the soil environment healthier and more friendly to life (Wilson, 2004).

The rate and nature of weathering as well as the quality and quantity of weathering products depend on many factors such as the nature of the given rock and its mineral composition, climate and hydrologic conditions, vegetation cover, and time (Wilson, 2004). In addition, the rate of weathering varies in different parts of the weathering profile. Usually, the most intense weathering occurs in the uppermost soil horizons as a result of the highest content of organic acids and the highest activity of biota (Righi et al., 1999; Egli et al., 2001, 2008; Wilson, 2004; Skiba, 2007) and gradually diminishes with depth. The rate and nature of weathering in the soil environment both also depend on the size, internal structure, and occurrence of defects and planes of weakness in crystals as well as the chemical composition of primary minerals forming the parent material of the soil (Wilson, 2004).

Andesite is a fine-grained, extrusive igneous rock of volcanic origin, which often occurs in the form of intrusions such as dykes and sills. It consists mainly of plagioclase, pyroxene, and hornblende. In addition, andesite frequently contains accessory minerals such as

Figure 1. Location of the studied soil profiles.

magnetite, biotite, apatite, ilmenite, and zircon (Best, 2002; Gill, 2010; Winter, 2010). Andesite is characterized by aphanitic and porphyritic texture, and according to the Total Alkali Silica (TAS) classification of volcanic rocks, it includes an average amount of silica (57% to 63%), more than basalt and less than dacite (Best, 2002; Gill, 2010; Winter, 2010).

In spite of the fact that the occurrence of andesite in the Earth's surface is very common and among extrusive igneous rocks only basalts are more widespread (Bolewski & Parachoniak, 1988; Gill, 2010; Winter, 2010), very little is known about the weathering of andesite and soils formed from its residue in a moderately humid climate (Colman, 1982; Glassman, 1982), as most studies on andesite weathering are conducted in the tropics (Mulyanto et al., 1999; Mulyanto & Stoops, 2003; Patino et al., 2003; Sak et al., 2010; Schopka et al., 2011; Ma et al., 2012; Opfergelt et al., 2012a, 2012b), in arid or semi-arid climate conditions (Colman, 1982; Tonui et al., 2003), and in Mediterranean climate areas (Hendricks & Whittig, 1968; Colman, 1982).

The main aim of this study is to describe andesite weathering and soil formation in a moderately humid climate area in the Western Carpathians in southern Poland based on physical, chemical, and micromorphologic properties of selected soil profiles.

2. MATERIALS AND METHODS

2.1. Study area

The study was conducted in the Western Carpathians in southern Poland (Fig. 1). The study area is located along the boundary between the Outer and Central Western Carpathians and is characterized by quite complex geology. The northern and central parts of the study area are formed of interbedded sandstone, mudstone, and shale (so-called Carpathian flysch) classified as the "Magura Nappe," while the southern part is composed of Jurassic-Cretaceous calcareous rocks such as limestone and marl and covered by Paleogene clastic rocks including sandstone and conglomerates (Książkiewicz, 1972). The studied rocks became intruded by several andesitic dykes and sills during the Miocene (12.5-10.8 Ma) outcropping on Mt. Wżar (766 m a.s.l.), Mt. Bryjarka (679 m a.s.l.), Mt. Jarmuta (795 m a.s.l.), and at many other sites in close proximity to the small towns of Krościenko nad Dunajcem and Szczawnica (Birkenmajer, 1956, 1957, 1962; Książkiewicz, 1972; Birkenmajer & Pécskay, 2000). Cambisols and Leptosols developed from Carpathian flysch residue prevail in the study area and its close vicinity (Skiba & Drewnik, 2003). The study area is characterized by moderately humid climate conditions, with mean annual air temperature ranging from 5 to 6°C and total annual precipitation ranging from 700 to 850 mm (Obrębska-Starklowa et al., 1995). The landscape of the study area is characterized by a mosaic of broadleaf forests (mainly *Dentario glandulosae-Fagetum*), grasslands (*Anthylii - Trifolietum montani* or *Gladiolo - Argostietum*), and agricultural crops (Balon et al., 1995; Towpasz & Zemanek, 1995).

2.2. Field and laboratory methods

Six representative soil profiles were selected for detailed study. The geographic location of the studied soil profiles is shown in Figure 1.

Table 1. Detailed information about study sites and classification of the soils

Profile	Location	Geomorphology	Vegetation	Classification according to WRB [a]
Wżar 1	49°56'42N; 20°56'51E; 225 m a.s.l.	Gentle, concave, lower part of slope (<5°); exposure W	Grassland (*Anthylii - Trifolietum montani*)	Eutric Leptic Cambisol Loamic
Wżar 2	49°55'10N; 20°56'43E; 255 m a.s.l.	Gentle, convex, upper part of slope (<5°); exposure NE	Grassland (*Anthylii - Trifolietum montani*)	Eutric Leptic Regosol Siltic
Wżar 3	49°55'20N; 20°56'35E; 236 m a.s.l.	Gentle, concave, lower part of slope (<3°); exposure NE	Grassland (*Anthylii - Trifolietum montani*)	Eutric Leptic Cambisol Siltic
Wżar 4	49°55'50N; 20°57'50E; 345 m a.s.l.	Almost flat summit of hill (<2°); exposure NW	Grassland (*Anthylii - Trifolietum montani*)	Eutric Leptic Regosols Siltic
Bryjarka	49°58'03N; 20°29'25E; 255m a.s.l.	Gentle, convex, middle part of slope (<5°); exposure S	Forest (*Dentario glandulosae-Fagetum*)	Eutric Umbric Lithic Leptosol Loamic Humic
Jarmuta	49°58'15N; 20°29'05E; 260 m a.s.l.	Gentle, convex, upper part of slope (<5°); exposure NW	Forest (*Dentario glandulosae-Fagetum*)	Eutric Skeletic Leptic Cambisol Loamic Protocalcic

[a] - IUSS Working Group WRB, 2014.

The profiles were described in the field and sampled. In addition to standard samples, undisturbed soil samples were collected using Kubiëna boxes for the purpose of micromorphologic studies. Unweathered rock samples from each of the study sites were collected as well. According to the Total Alkali Silica (TAS) classification of volcanic rocks, samples collected from Mt. Wżar represent basaltic andesite, while samples collected from Mt. Bryjarka and Mt. Jarmuta represent andesite. The studied samples were collected from each soil horizon and stored in plastic bags and air dried upon arrival at the laboratory. The samples were later gently crushed, and sieved through a 2 mm sieve. The texture of the fine earth material (fraction < 2 mm) was determined using a set of sieves (sand fractions) and via a hydrometer method (silt and clay fractions) (Gee & Bauder, 1986). Soil pH was measured potentiometrically in distilled water at a 1:2.5 ratio (Thomas, 1996) and carbonate content was determined by means of a volumetric calcimeter method (Loeppert & Suarez, 1996). Soil organic carbon content was determined using a modified Tyurin titrimetric technique (Nelson & Sommers, 1996) and total nitrogen content was determined by means of a Vario Micro Cube CHN elemental analyzer. The chemical composition of the fine earth material (fraction < 2 mm) and fresh rock fragments was determined using Inductively Coupled Plasma-Emission Spectrometry (ICP − ES). The chemical index of alteration (CIA) was calculated according to Nesbitt & Young (1982). The chemical index of weathering (CIW) was calculated according to Harnois (1988). The plagioclase index of alteration (PIA) was calculated according to Fedo et al., (1995). Finally, the weathering index of Parker (WIP) was calculated according to Parker (1970). Exchangeable cation (Ca^{2+}, Mg^{2+}, K^+, Na^+) content was measured using Flame Atomic Absorption Spectrometry (FAAS) after extraction with 1M ammonium acetate at pH = 7 (Sumner & Miller, 1996), and the concentration of exchangeable in 1M KCl H^+ and Al^{3+} (Summer, 1992) was determined by titration of extracts (after boiling for 10 s) with 0.1 M NaOH in the presence of phenolphthalein. Soils were classified according to the WRB system (IUSS Working Group WRB 2014). Micromorphologic observations were carried out under a Nikon Eclipse 50iPOL polarizing microscope using thin sections. In this study, terminology given by Stoops (2003) was used.

3. RESULTS AND DISCUSSION

3.1. Soil morphology and classification

The location and classification of the studied soil profiles according to the WRB system (IUSS Working Group WRB 2014) are shown in Table 1, while a field description of the morphology of the studied soil profiles is summarized in Table 2. The majority of the soils are thin or very thin, with a thickness between 8 and 65 cm.

Only one profile (Wżar 3) was deeper, with a thickness of 100 cm. Two soil profiles (Wżar 4 and Jarmuta) exhibit lithologic discontinuities, which is a quite common occurrence in soils in the Carpathians (Kacprzak & Derkowski, 2007; Kacprzak et al., 2015) as well as in other mountain areas (Lorz & Phillips, 2006; Phillips & Lorz, 2008). The surface soil horizons of the studied soils (A, Ak) are characterized by fine and very fine granular and subangular blocky structure, soft or slightly hard consistence, presence of many roots, and usually low content of rock fragments – up to 15%, with the exception of the Jarmuta profile where the rock fragment content in the surface horizon is 40%. The boundary between the A or Ak horizons and underlying AB, Bw or BC horizons is usually clear. The AB, Bw, and BC horizons exhibit most often subangular or angular blocky structure, slightly hard or hard consistence, occurrence of many roots, and higher content of rock fragments (up to 60%). The boundaries between these horizons are usually gradual (Table 2). The lowermost C or Ck horizons exhibit a massive structure, hard or very hard consistence, complete absence or presence of only a few roots, and variable content of rock fragments (from 10 to 70%).

Three of the studied soils were classified as Cambisols (Wżar 1, Wżar 3, Jarmuta profiles), while the next two profiles were classified as Regosols (Wżar 2 and 4 profiles), and the last studied soil profile was classified as a Leptosol (Bryjarka profile), which indicates that the studied soils are relatively weakly developed due to their hard and highly resistant to weathering andesitic bedrock.

3.2. Physical and chemical properties

Selected physical and chemical properties of the studied soil profiles are shown in Table 3. Most of the studied soils are characterized by silt loam or loam texture, but in selected cases (Bryjarka and Jarmuta profiles) also sandy loam texture (Table 3). Sand fraction content ranges from 32% to 63% and the silt fraction is between 28% and 65%. Clay fraction content is low and ranges from 3% to 13% (Table 3). In general, the clay fraction exhibits a very slight increasing trend with increasing soil depth. All the studied soils, with the exception of the Jarmuta profile, are characterized by acidic or slightly acidic pH, which gradually increases with increasing depth.

Table 2. Field description of morphology of the soils

Horizon	Depth (cm)	Structure	Consistence	Roots	Rock fragments (%)	Boundary
Wżar 1						
A	0-6	Granular and subangular blocky	Slightly hard	Many	15	Clear
Bw	6-40	Sub- and angular blocky	Slightly hard	Many	30	Gradual
BC	40-65	Sub- and angular blocky	Hard	Few	50	---
R	<65	n.a.	n.a.	n.a.	n.a.	n.a.
Wżar 2						
A	0-10	Granular and subangular blocky	Soft	Many	15	Gradual
BC	10-35	Sub- and angular blocky	Slightly hard	Many	30	---
R	<35	n.a.	n.a.	n.a.	n.a.	n.a.
Wżar 3						
Oi	0-3	n.a.	n.a.	n.a.	n.a.	n.a.
A	3-10	Granular and subangular blocky	Soft	Many	5	Clear
AB	10-22	Sub- and angular blocky	Slightly hard	Many	10	Gradual
Bw1	22-35	Sub- and angular blocky	Slightly hard	Many	20	Gradual
2Bw2	35-55	Sub- and angular blocky	Hard	Few	10	Gradual
2BC	55-70	Sub- and angular blocky	Hard	Few	10	Gradual
3C	70-100	Massive	Hard	Absence	10	---
R	<100	n.a.	n.a.	n.a.	n.a.	n.a.
Wżar 4						
Oi	0-4	n.a.	n.a.	n.a.	n.a.	n.a.
A	4-14	Granular and subangular blocky	Slightly hard	Many	5	Clear
AB	14-35	Granular and angular blocky	Slightly hard	Many	30	Gradual
BC	35-60	Granular and angular blocky	Slightly hard	Few	40	---
R	<60	n.a.	n.a.	n.a.	n.a.	n.a.
Bryjarka						
Oe	0-5	n.a.	n.a.	n.a.	n.a.	n.a.
A	5-8	Granular and subangular blocky	Soft	Many	15	---
R	<8	n.a.	n.a.	n.a.	n.a.	n.a.
Jarmuta						
Ak	0-8	Granular and single grain	Soft	Many	40	Clear
2Bwk	8-32	Sub- and angular blocky	Slightly hard	Many	60	Gradual
2Ck	32-48	Massive	Very hard	Few	70	---
R	<48	n.a.	n.a.	n.a.	n.a.	n.a.

n.a. - Not analyzed.

Values of pH of the soils range from 5.2 to 6.7 (Table 3). This is related to a lack of carbonate in the parent material and a moderately humid climate, which is responsible for the leaching of soils. The lowest pH of the surface soil horizons of the studied soils is associated with the highest organic matter content (Table 3) and highest content of organic acids in these particular horizons. On the other hand, the Jarmuta profile features an alkaline pH (7.4 to 8.3) indicating the presence of carbonate in this profile. The carbonate content in this soil profile increases with increasing depth from 8.5% in the Ak horizon to 11.0% in BCk horizon (Table 3). According to Jurewicz et al. (2007), the presence of carbonate in the form of flowstone-like calcite filling the fractures of andesites in Mt. Jarmuta is related to tectonic activity in this area (~2.5 to 6.5 ka) and crystallization of calcite under low temperature conditions.

All the studied soils feature a quite high content of organic carbon (SOC) as well as low total nitrogen (Ntot) content in their uppermost horizons, i.e. from 2.72 to 11.00% and from 0.24 to 0.78%, respectively (Table 3). In addition, lower soil horizons in the Wżar 2, Wżar 3, and Wżar 4 profiles also feature considerable organic carbon content. The highest SOC and Ntot content in the uppermost horizons of the studied soils is present and gradually decreases with increasing soil depth. The C/N ratio for all the studied soils ranges from 6 to 14, indicating a high degree of organic matter decomposition. The chemical composition of the soils and unweathered andesitic rocks (R) obtained from Mt. Wżar, Mt. Bryjarka, and Mt. Jarmuta is shown in Table 4.

Table 3. Physical and chemical properties of the soils

Horizon	Depth (cm)	Sand (%)	Silt	Clay	Texture according to USDA [a]	pH (H_2O)	SOC [b] (%)	Ntot [c]	C/N	$eqCaCO_3$ (%)
					Wżar 1					
A	0-6	48	45	7	Loam	5.8	3.39	0.26	13	0.0
Bw	6-40	51	41	8	Loam	6.4	0.74	0.05	14	0.0
BC	40-65	50	42	8	Loam	6.7	0.52	0.04	13	0.0
R	<65	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
					Wżar 2					
A	0-10	41	52	7	Silt loam	5.6	4.35	0.40	11	0.0
BC	10-35	34	57	9	Silt loam	6.0	2.18	0.21	10	0.0
R	<35	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
					Wżar 3					
Oi	0-3	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
A	3-10	33	59	8	Silt loam	5.2	6.03	0.44	14	0.0
AB	10-22	37	56	7	Silt loam	5.4	3.88	0.31	12	0.0
Bw1	22-35	34	57	9	Silt loam	5.6	1.54	0.12	13	0.0
2Bw2	35-55	46	43	11	Loam	5.9	0.67	0.05	12	0.0
2BC	55-70	52	39	9	Loam	6.2	0.50	0.04	11	0.0
3C	70-100	37	50	13	Silt loam	6.2	0.71	0.08	10	0.0
R	<100	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
					Wżar 4					
Oi	0-4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
A	4-14	40	57	3	Silt loam	5.4	6.61	0.50	13	0.0
AB	14-35	32	65	3	Silt loam	5.6	3.76	0.28	13	0.0
BC	35-60	36	57	7	Silt loam	5.9	1.63	0.14	12	0.0
R	<60	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
					Bryjarka					
Oe	0-5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
A	5-8	59	38	3	Sandy loam	5.5	11.00	0.78	14	0.0
R	<8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
					Jarmuta					
Ak	0-8	52	39	9	Loam	7.4	2.72	0.24	11	8.5
2Bwk	8-32	63	28	9	Sandy loam	8.1	0.37	0.05	7	9.7
2Ck	32-48	58	30	12	Sandy loam	8.3	0.32	0.05	6	11.0
R	<48	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

[a] - United States Department of Agriculture; [b] - Soil organic carbon; [c] - Total nitrogen; n.a. - Not analyzed.

Table 4. Chemical composition of the soils and their unweathered parent rocks, and chemical indexes of weathering

Horizon	Depth (cm)	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	CIA[a]	CIW[b]	PIA[c]	WIP[d]
		(%)											
Wżar 1													
A	0-6	54.1	14.8	6.2	2.5	3.8	1.9	1.8	0.8	66	72	70	3355
Bw	6-40	57.6	15.6	6.5	2.7	4.1	2.0	2.0	0.8	66	72	69	3594
BC	40-65	57.9	15.8	6.6	2.7	4.1	2.1	2.0	0.8	66	72	69	3674
R	<65	54.6	18.6	7.2	2.9	7.9	3.7	1.7	0.7	58	62	59	4951
Wżar 2													
A	0-10	46.0	16.7	7.6	3.0	4.3	2.0	1.7	0.9	67	73	70	3487
BC	10-35	47.4	17.7	7.9	3.2	4.5	2.1	1.8	0.9	68	73	71	3640
R	<35	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Wżar 3													
Oi	0-3	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
A	3-10	50.46	14.5	6.2	2.1	2.9	1.7	1.7	0.9	70	76	74	3007
AB	10-22	52.5	15.4	6.5	2.2	3.1	1.8	1.8	0.9	70	76	74	3178
Bw1	22-35	54.2	16.3	7.0	2.5	3.5	2.0	1.9	0.9	69	75	72	3405
2Bw2	35-55	51.8	17.5	7.7	2.9	4.3	2.2	1.8	0.9	68	73	71	3652
2BC	55-70	51.8	17.6	7.7	3.0	4.4	2.2	1.7	0.9	68	73	71	3591
3C	70-100	52.7	17.4	7.5	2.7	3.7	2.1	1.8	0.9	70	75	73	3452
R	<100	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Wżar 4													
Oi	0-4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
A	4-14	47.9	15.8	6.3	1.8	3.3	2.2	1.6	0.8	69	74	72	3179
AB	14-35	50.8	17.2	6.8	1.9	3.5	2.4	1.7	0.9	69	75	73	3435
BC	35-60	53.5	18.0	7.0	1.9	3.6	2.5	1.8	0.9	69	75	73	3644
R	<60	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Bryjarka													
Oe	0-5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
A	5-8	46.7	13.7	4.6	0.9	2.5	2.1	1.2	0.5	70	75	73	2618
R	<8	60.3	18.4	5.5	1.7	5.7	4.1	1.6	0.5	62	65	63	4612
Jarmuta													
Ak	0-8	57.4	11.7	4.4	2.7	4.6	1.0	2.4	0.5	60	68	63	3394
2Bwk	8-32	60.0	13.9	5.2	2.0	5.7	1.8	2.1	0.5	59	65	61	3731
2Ck	32-48	57.2	13.6	5.0	2.3	7.3	1.6	2.2	0.5	55	61	56	3936
R	<48	60.1	18.3	5.0	1.1	6.3	4.1	1.5	0.5	61	64	62	4514

[a] - Chemical index of alteration; [b] - Chemical index of weathering; [c] - Plagioclase index of alteration; [d] - Weathering index of Parker; n.a. - Not analyzed.

All the studied rocks and soil material are composed mainly of three constituents: SiO_2, from 46.0% to 60.0%, with a mean of 52.8% in soils, and from 54.6% to 60.3%, with a mean of 58.3% in unweathered rocks; Al_2O_3, from 11.7% to 18.0%, with a mean of 15.8% in soils, and from 18.3% to 18.6%, with a mean of 18.4% in unweathered rocks; Fe_2O_3, from 4.4% to 7.9%, with a mean of 6.5% in soils, and from 5.0% to 7.2%, with a mean of 5.9% in unweathered rocks. Magnesium oxide, CaO, Na_2O, and K_2O are present in lower amounts. The mean content of CaO and Na_2O in unweathered andesites is higher than the mean content of these oxides in soil profiles (i.e. 6.7 and 4.0% in andesites, respectively, versus 4.1 and 2.0% in soil material, respectively). On the other hand, the mean content of MgO and K_2O is higher in soils than in unweathered andesitic rocks (i.e. 2.4 and 1.8% in soils, respectively, versus 1.9 and 1.6% in rocks, respectively). The content of TiO_2, P_2O_5, and MnO as well as other oxides remains below 1% (Table 4), and differences in the mean content of these oxides in soils and unweathered andesites are very similar, with the exception of TiO_2, whose mean content is clearly higher in soils than in unweathered andesites. The chemical composition of unweathered andesites and soils clearly indicates that during the weathering of andesites in a soil environment, certain elements such as Si, Al, Ca, and Na become depleted due to leaching in a humid climate (Colman, 1982; Ma et al., 2012; Opfergelt et al., 2012a; Musielok & Drewnik, 2016). According to Fraysse et al., (2006, 2009), Si previously taken up by plants and then returned to the soil after the death of the plant is more soluble than Si from minerals, and can be easily leached from the soil. On the other hand, weathering is responsible for increasing TiO_2 content in soils in comparison with unweathered andesites, as this particular oxide, even in humid climate conditions, remains relatively immobile due to its occurrence in highly resistant minerals such as rutile, ilmenite, and anatase (Ma et al., 2012; Musielok & Drewnik, 2016).

Chemical composition, chemical index of alteration and weathering (CIA and CIW), plagioclase index of alteration (PIA), and weathering index of Parker (WIP) all indicate that the soil material from all the studied profiles (except the Jarmuta profile) is more weathered in comparison with andesitic bedrock (Table 4).

This is not true of the Jarmuta profile, because this soil profile is enriched in carbonate by meteoric water during the Holocene (Jurewicz et al., 2007). Weathering is most frequently evidenced by WIP and CIW, whose mean values for bedrock are 4692 and 61, respectively, and for soil material, 3443 and 72, respectively. The mean value of CIA is 60 for andesitic bedrock and 67 for soil profiles.

The mean value of PIA is 61 for andesitic bedrock and 70 for soil profiles, indicating that plagioclases are more strongly weathered in soils in comparison with andesitic rocks (Table 4). The mean value of WIP is 3443 for soils and 4692 for unweathered andesite bedrock. Differences between the values of CIA, CIW, PIA, and WIP for different soil horizons are negligible, which is most likely related to the thin or very thin soil profiles studied.

All the studied soils exhibit high base saturation throughout the entire profile, which ranges from 74% to 100% (Table 5). Calcium (Ca^{2+}) clearly

Table 5. Exchangeable cations, exchangeable acidity, cation exchange capacity, and base saturation of the soils

Horizon	Depth	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	H_w [a]	H^{+}	Al^{3+}	CEC [b]	BS [c]
	(cm)	cmol (+) * kg^{-1}								(%)
Wżar 1										
A	0-6	17.98	3.53	0.29	0.07	0.61	0.35	0.26	22.48	97
Bw	6-40	17.77	2.85	0.10	0.11	0.44	0.22	0.22	21.27	98
BC	40-65	16.90	2.95	0.06	0.16	0.22	0.18	0.04	20.29	99
R	<65	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Wżar 2										
A	0-10	18.32	3.51	0.49	0.09	1.31	0.57	0.74	23.72	94
BC	10-35	21.23	3.39	0.16	0.13	1.44	0.48	0.96	26.34	95
R	<35	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Wżar 3										
Oi	0-3	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
A	3-10	15.52	3.69	0.49	0.06	1.72	0.48	1.24	21.47	92
AB	10-22	16.82	3.83	0.39	0.08	1.09	0.44	0.65	22.21	95
Bw1	22-35	19.83	3.57	0.06	0.13	0.48	0.31	0.17	24.08	98
2Bw2	35-55	24.18	4.32	0.04	0.17	0.39	0.39	0.00	29.10	99
2BC	55-70	24.71	4.84	0.04	0.17	0.39	0.39	0.00	30.15	99
3C	70-100	23.49	4.86	0.03	0.17	0.39	0.39	0.00	28.95	99
R	<100	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Wżar 4										
Oi	0-4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
A	4-14	12.15	2.44	0.21	0.07	0.48	0.09	0.39	15.35	97
AB	14-35	13.45	1.83	0.10	0.14	0.22	0.09	0.13	15.74	99
BC	35-60	13.28	1.75	0.04	0.17	0.13	0.04	0.09	15.37	99
R	<60	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Bryjarka										
Oe	0-5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
A	5-8	8.75	1.34	0.45	0.06	3.68	3.06	0.62	14.29	74
R	<8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Jarmuta										
Ak	0-8	19.62	1.80	0.35	0.02	0.04	0.04	0.00	21.83	100
2Bwk	8-32	17.68	1.41	0.17	0.02	<0.04	<0.04	<0.04	19.28	100
2Ck	32-48	20.04	1.31	0.18	0.02	<0.04	<0.04	<0.04	21.56	100
R	<48	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

[a] - Exchangeable acidity; [b] - Cation exchange capacity; [c] - Base saturation; n.a. - Not analyzed.

prevails as the exchangeable cation (8.75 to 24.71 $cmol_c\ kg^{-1}$), and its content generally increases with depth (Wżar 2 and Wżar 3 profiles) or remains almost evenly distributed throughout the soil profile (Wżar 1, Wżar 4, and Jarmuta profiles). The prevalence of Ca^{2+} is most likely associated with the weathering of plagioclase, hornblende, and augite and the liberation of this cation from their crystal lattices. The amount of exchangeable Mg^{2+} is clearly lower than the available Ca^{2+} content, and ranges from 1.31 to 4.86 $cmol_c\ kg^{-1}$ (Table 5). The Mg^{2+} content is the highest in the uppermost horizons and decreases with depth, with the exception of the Wżar 4 profile where an opposite trend occurs, and this may be related to biocycling. Most likely, the lower content of Mg^{2+} in comparison with Ca^{2+} is related to the fact that Mg^{2+} is present only in hornblende and augite, and not in plagioclase. Micromorphologic studies (see below) have shown that the content of plagioclase is higher than the content of hornblende and augite in the studied soils and andesitic bedrock. This is in accordance with the mineral composition of andesite from Mt. Wżar discussed by Youssef (1978). The content of exchangeable K^{+} and Na^{+} is very low and ranges from 0.03 to 0.49 and from 0.02 to 0.17 $cmol_c\ kg^{-1}$, respectively (Table 5). The highest content of K^{+} occurs in the uppermost horizons, and this may be also related to biocycling (Jobbágy & Jackson, 2001; 2004; Musielok & Drewnik, 2016) as it is likely in the case of Mg^{2+}. The highest content of Na^{+} occurs in the lowermost horizons, except for the Jarmuta profile, where the content of Na^{+} is the same throughout the entire profile, as this particular cation is not very important in plant nutrition, and it is the most mobile in the soil environment (Colman, 1982; Sposito, 1989; Jobbágy & Jackson, 2001; 2004). Exchangeable acidity in the studied soil profiles ranges from <0.04 to 3.68 $cmol_c\ kg^{-1}$, being the highest in the uppermost horizons and then regularly decreasing with depth (except for Wżar 2 and Jarmuta profiles) (Table V). The cation exchange capacity (CEC) ranges between 14.29 and 30.15 $cmol_c\ kg^{-1}$ and does not exhibit a consistent trend in the studied soil profiles (Table 5). In certain profiles, the highest CEC occurs in the uppermost horizon (Wżar 1 profile), but in other soils (Wżar 2 and Wżar 3 profiles), the highest CEC occurs in the lower part of the profile. CEC for the Wżar 4 and Jarmuta profiles is almost the same throughout the entire profile (Table 5).

3.3. Micromorphologic properties

Soils developed from andesite residue are characterized mainly by fine and very fine granular and crumb microstructure in surface soil horizons (A, Ak) and fine to medium subangular blocky microstructure in Bw and BC horizons (Figs. 2A, 2B). In certain cases, in Bw and BC horizons, a fine to medium angular blocky microstructure is also present (Figs. 2C, 2D). According to the literature (Stoops 2007), the origin of the granular microstructure may be related to high biological activity and/or physical processes such as wetting/drying or freezing/thawing cycles. The presence of many roots and organic residues indicates that biological activity in the studied soils is very high. All the studied soil profiles exhibit high porosity, especially in the upper soil horizons (A, AB). Prevailing types of voids in A, Bw, and BC horizons are complex packing voids with occasionally occurring fissures, channels, and chambers (Fig. 2).

The coarse mineral material of the groundmass is composed of slightly, moderately, and strongly weathered fragments and angular fragments of andesite as well as grains of plagioclase sometimes characterized by strong zonality and lower amounts of hornblende and augite. In addition, there occur a few grains of quartz and very few flakes of biotite as well as opaque minerals. Such mineral composition is inherited from andesitic bedrock, because the same minerals – and in similar proportions – were determined by Youssef (1978) in andesite from Mt. Wżar. In surface soil horizons, fragments of andesite exhibit the strongest evidence of physical and chemical weathering, with many cracks and rusty and/or brownish-red crystals of hornblende and augite indicating oxidation of iron (Colman 1982) (Fig. 3). Crystals of hornblende exhibit very often irregular linear alteration along lines of cleavage (Fig. 4).

Additionally, many fragments of andesite and coarser mineral grains indicate the presence of weathering rims, which are composed mainly of iron hydroxides, clay minerals together with iron hydroxides, and sometimes also organic matter – especially in the A horizons (Figs. 3 and 5). This is consistent with Colman (1982) who observed similar rims on weathered fragments of andesites and basalts in Western USA.

The micromass of the studied soils is composed mainly of brown or brownish-gray humus, rusty or brownish-rusty iron hydroxides, and small amount of yellowish clay minerals characterized by undifferentiated and speckled b-fabric in A horizons, and rusty or brownish-rusty iron hydroxides and yellowish clay minerals characterized by speckled and granostriated b-fabric in Bw and BC horizons.

All the studied soils are characterized by a high amount of plant and animal residue indicating high biological activity of the soils. The organic residues exhibit various types of alteration including deformation, browning, blackening, and impregnation with iron hydroxides. This indicates that the organic fragments show various stages of decomposition. In addition, in certain profiles (Wżar 2 and Bryjarka 1), many fragments of charcoal are also present.

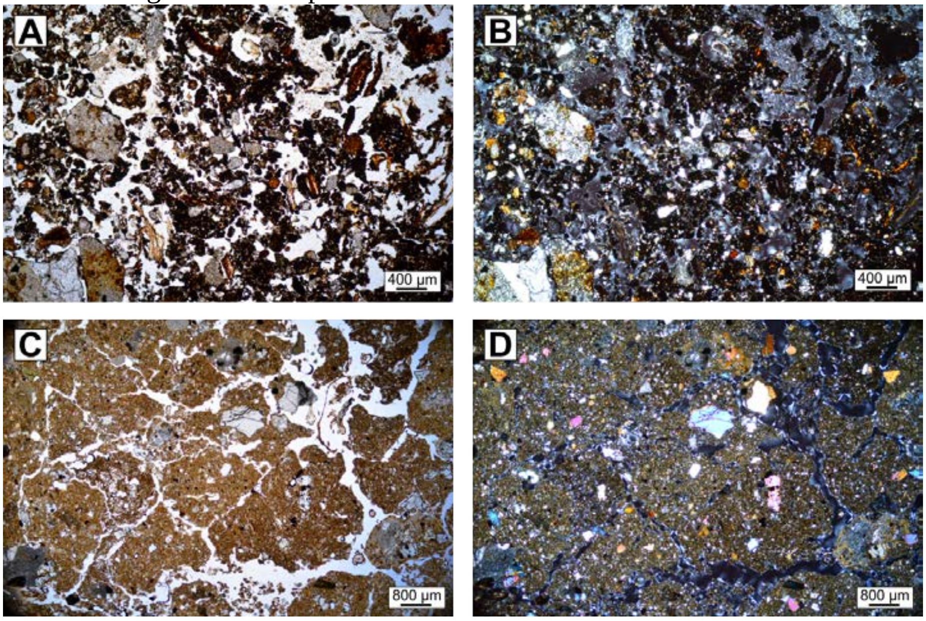

Figure 2. Granular and crumb microstructure in A horizon of the Bryjarka profile (A, B); angular and subangular blocky microstructure in BC horizon of the Wżar 2 profile (C, D); A, C - plane polarized light; B, D – crossed polarized light.

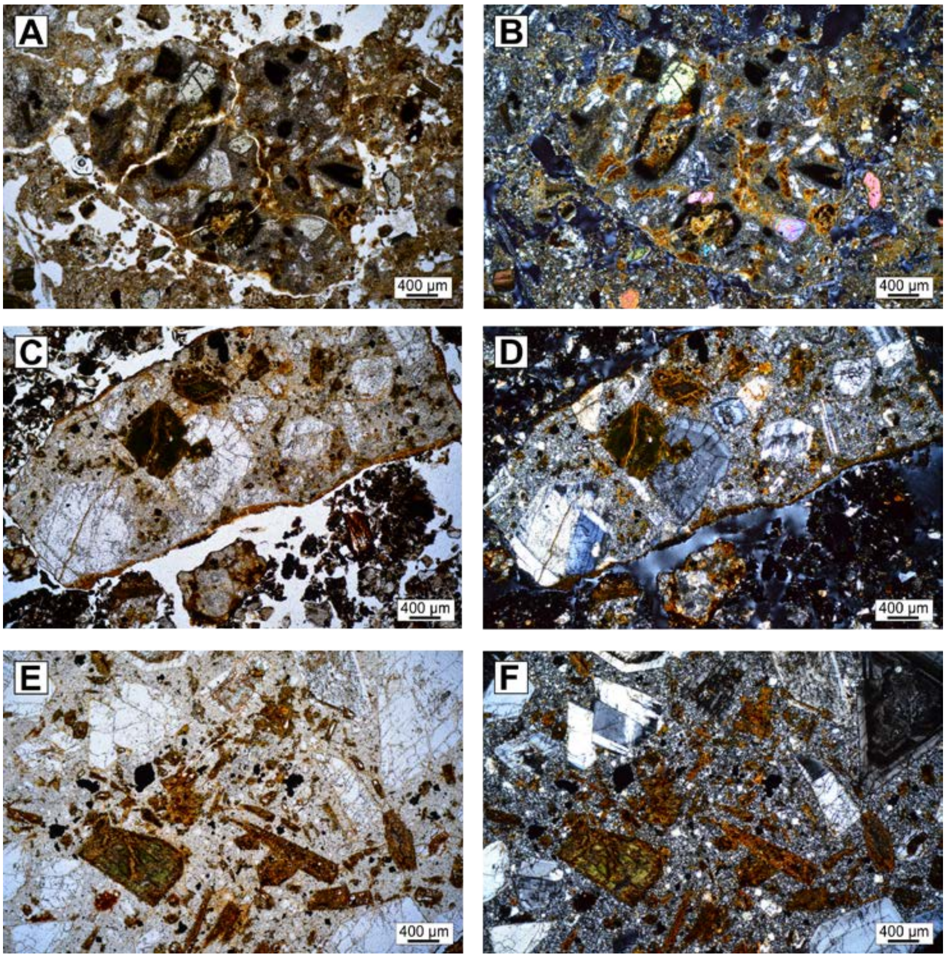

Figure 3. Physically and chemically weathered andesite fragments in the A horizon of the Wżar 1 profile (A, B) and in A horizon of the Bryjarka profile (C-F); A, C, E - plane polarized light; B, D, F - crossed polarized light.

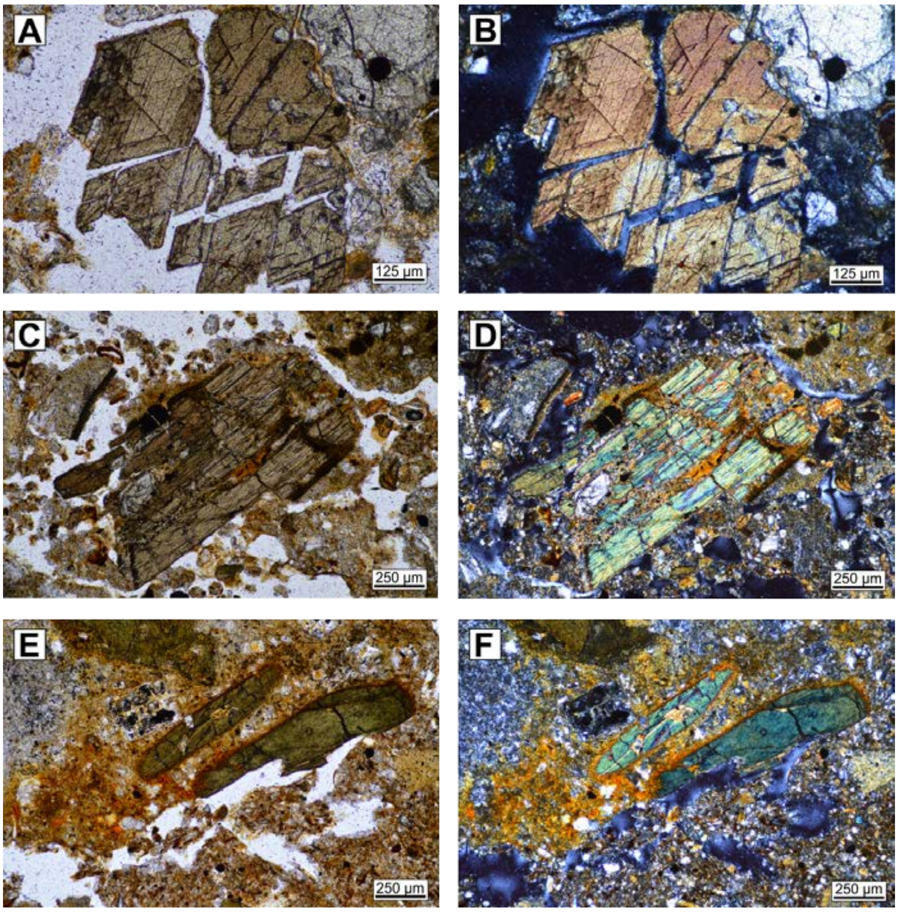

Figure 4. Physically and chemically weathered crystals of hornblende in the A horizon of the Wżar 1 profile; A, C, E - plane polarized light; B, D, F - crossed polarized light.

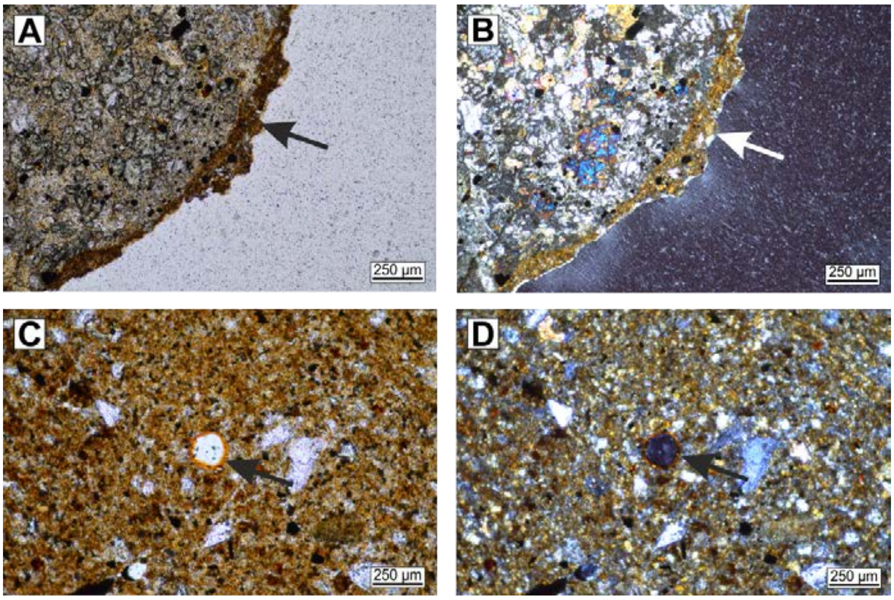

Figure 5. Iron hydroxide-clay coating on andesite fragments (arrow) in A horizon of the Wżar 2 profile (A, B) and clay coating in BC horizon of the Wżar 2 profile (C, D); A, C - plane polarized light; B, D – crossed polarized light.

Iron hydroxide and iron hydroxide-clay coatings occurring on andesite fragments and coarse mineral grains are the most common pedofeatures in all of the studied soils (Figs. 5A, 5B). In addition, in the Bw horizon of the Wżar 1 and the BC horizon of the Wżar 2 profiles, very few clay coatings were observed, indicating that some part of the finest particles is translocated downward due to a moderately humid climate and lack of carbonate in the soils (Figs. 5C, 5D) (Szymański et al., 2011, 2012; Drewnik et al., 2014; Nikorych et al., 2014).

4. CONCLUSIONS

Soils developed from andesite in the Carpathians are characterized by variable thickness, but usually are thin or very thin, show weak development due to hard and highly resistant to weathering andesitic bedrock, and are classified as Cambisols, Regosols, and/or Leptosols according to the WRB classification system. The studied soils usually exhibit loamy texture, acidic or slightly acidic pH, lack of carbonates, quite high content of organic carbon, and low content of total nitrogen.

All the studied soils exhibit high base saturation throughout the entire profile, and Ca^{2+} clearly prevails as the exchangeable cation, which is most likely related to the weathering of plagioclase, hornblende, and augite. The andesite weathering and soil formation in a moderately humid climate are reflected by significant depletion of SiO_2, Al_2O_3, CaO, and Na_2O from soils in relation to unweathered andesite bedrock. The chemical index of alteration and weathering (CIA and CIW) and plagioclase index of alteration (PIA) as well as weathering index of Parker (WIP) all indicate that soil material obtained from all the studied profiles, except the Jarmuta profile, which is enriched in carbonate by meteoric water during the Holocene, is distinctively more weathered in comparison with andesitic bedrock. However, these chemical indexes do not show distinctive differences in weathering degree of soil material between different soil horizons, which is most likely related to the excessively thin soil profiles used in this study and/or the occurrence of lithologic discontinuities in selected profiles. Micromorphologic observations indicate that during the process of weathering, many fragments of andesite undergo cracking and iron in the phenocrysts of hornblende and augite undergoes oxidation. The crystals of hornblende exhibit very often irregular linear alteration along lines of cleavage. Additionally, many fragments of andesite and coarser mineral grains are characterized by the presence of weathering rims, which are composed mainly of iron hydroxides, clay minerals together with iron hydroxides, and sometimes also organic matter.

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