MINERALOGY AND GEOCHEMISTRY OF ANDOSOLS FROM GURGHIU MOUNTAINS (PART I)

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Have been studied 13 andosol samples from two profiles (Gurghiu Mountains), from chemical and mineralogical point of view. The field surveys and chemical-mineralogical analysis have evidenced that the andic character of studied soils, the andesitic nature of parental material by eruptive type and a different spatial distribution of andosols towards to the underlined in previous studies. The andosols from Gurghiu Mountains have been formed on andesitic material arise from two sources, in two successive steps: (i) in first step on basis of piroclastes materials (ash and volcanic glass), (ii) in second step on basis of andesitic agglomerates. The frequent occurrence form of piroclastes in studied andosols (> 90 %) is the granules associated with other mineral and organic components: (i) macroscopic associations (agglomerates) and (ii) colloidal microscopic associations (macromicelles). Over 80 % from amorphous clay minerals (imogolite, allophane) and from humus are included in allophano-humic associations. The structure and the ratio between the components of allophano-humic complexes varied in function of allophonic or non-allophanic character of andosols. Another characteristic of these andosols is the existence of two types of allophanes and the specific way of association of these with humus and other mineral components of andosols: (i) allophone I (aluminous) characteristic to the non-allophanic andosols and (ii) allophone II (siliceous) characteristic to the allophanic soils. Between these two forms of allophane is a dynamic equilibrium, conditioned by pH, organic matter content and thermodynamic activity of Al, Si and Fe. The transformation of allophane I in allophane II is accompanied by the retention of organic matter in allophanic-humic complexes, this having a protector role for allophane. At pH values lower than 5, the organic matter manifest and an anti-allophanic effect, which is traduced by destabilization of allophanic-humic associations, with the formation of metal (Al, Si) – humus complexes. In case of studied andosols the anti-allophanic effect is relative intense and has a regular character, dependent by the physic-chemical conditions from soil.

***Keywords**: andosol; andosolization; allofane.*

The andosols, according with WRB-SR (1998), represent a soil class with distinct morphology and unique chemical-mineralogical properties, determinate by the particularities of pedogenesis process (s.s *andosolization*) and by the geochemical evolution. These soils are formed in zones with volcanic deposits, in various climatic and relief conditions, representative being those developed by piroclastic products (ash and volcanic glass) [2, 17, 28, 31, 35]. According with most opinions, the mineralogical and physic-chemical particular properties of andosols are determined by the presence of amorphous minerals (allophane, imogolite, ferihidrite), of allophano-humic macromicelles associations and of Fe/Al-humus complexes.

The recent researches, propose the separation of andosols in two categories, allophanic and non-allophanic, on the basis of some, more or less conventional, criteria: (i) the composition of their colloids [13, 15, 31], (ii) the value of distribution ratio of Fe and Al between amorphous minerals (imogolite, allophane, ferihidrite) and Fe/Al-humus complexes [1, 4, 13, 24, 28, 35],(iii) the value of the ratio between Al extractable in pyrophosphate (Al_{piro}) and Al extractable in oxalate (Al_{oxa}) [3, 4, 13, 28, 31, 34, 35, 40], (iv) the dependence between cationic exchange capacity and pH [26, 30] etc. *Shoji et al.* (1993) and *Dahlgreen et al. (1994)* have show that in allophanic andosols, the active forms of Al and Fe are predominantly included in amorphous mineral phases (allophone, imogolite, ferihidrite), while in non-allophanic andosols these are bonded by organic matter (in special Fe/Al-humus complexes). These active forms of Al and Fe are preferential extractable in pyrophosphate. In agreement with this observation, it was showed that the Al_{piro} / Al_{oxa} ratio has values between 0.1-0.4 for allophanic andosols , and between 0.8-1.0 for non-allophanic andosols, respectively.

The first studies realized on andosols from Romania are the studies of *M.Opriş* (1964) in zone of Gutâi Mountains and *A.Conea* (1967) in Vlădeasa Mountains [17, 18, 31]. It is estimated that in Romania, the andosols have a surface of cca 180,000 ha (~ 0.7 % from surface of country), the higher surface being in Eastern Carpathians (Oaş-Gutâi, Ţibleş-Călimani-Harghita volcanic mountains) – cca 6.2 % from their surface. In Western Carpathians (Metaliferi Mountains, Vlădeasa Mountains) the andosols and andic soils have a weight by cca. 4 %, from their surface total. In mentioned zones, the andosols appear generally, at altitudinous of 900-1700 m, in Vlădeasa Mountains being mentioned their presence and at altitudinous higher than 1800 m [11, 12, 17, 18, 20, 27, 37]. The formation of andosols in Romania is connected by the two volcanic zones: (i) Western Carpathians – where appear the andosols developed by riolitic and/ or riodacitic piroclastic materials [17, 20, 31], (ii) Eastern Carpathians – where the parental material of andosols is predominantly andesitic and/ or dacitic [12, 16, 31].

The *Rusu et al. (2007)* researches on soils from Eastern Carpathians have show that, through the volcanic rocks and the product associated with volcanic eruption are on considerable surfaces (some times higher than 90 % - Călimani and Gurghiu Mountains), the formation conditions of andosols are practice limited to the perimeters with piroclastic rocks and derived deposits, where appear hialocristaline rocks (different varieties of andesites), vitreous rocks, inclusive deluvial mixtures from versants level. In this territory, the andosols have a total surface by 1573.50 km^2, which represent cca 23 % from soil cover of region. On the other hand, these studies have shows that spatial distribution and weight of anosols in different mountains from Eastern Carpathians are less than the values mentioned in literature from Romania. This observation is based on the fact that not all the time has been rigorous respected the taxonomical criteria, and that some evolution stages of some soils have been wrong evaluated. From these causes numerous varieties of andic districambosoils have been appreciated as andosols.

The research results regarding the genesis and pedogeochemical evolution of andosols presented in this paper are part of more ample study, including the utilization and mapping of the soils from the area of the Neogene volcanics from the Eastern Carpathians. The field surveys and chemical-mineralogical analyses have clearly evidenced the andic character of studied soils and the andesitic nature of some parental materials by eruptive nature. The mineralogy and chemistry of studied andosols are dominated by allophane and kaolinite, the quantitative ratio of these representing and a differentiation criteria between allophanic and non-allophanic types. The morphological and chemical-mineralogical characteristics of andosols, associations and mineral paragenesis, have evidenced several new aspects about the genesis and the evolution of these andosols.

MATERIAL AND METHOD

1. Work samples. The field surveys have been conducted in the last years (2002-2005) and the morphologic description and taxonomic classification have been realized according with the *Romanian Soil Taxonomy System (RSTS)* [21]. The field sampling has been conducted on pedogenetic horizons and on characteristic depths, from the organic horizons (Of, Oh) as well as the mineral ones (Aou, ABv, Bv, BC+R), on depth intervals of maximum 15 cm. For the explanation of the soil forming mechanisms we have selected three characteristic profiles from Gurghiu Mountains: MG.8 – Cambic Andosol and MG.16 – Cambic-histic Andosol (*tab.1*). The soil samples have been dried in the stove (3 hours at 60°C). After drying, the samples have been conducted to preliminary microscopic examinations, granulometric analysis and then grinded until the granulation was less than 0.100 mm. The analyses have done by average samples, according with specific work methodology [8, 19, 22]. For each sample was determined the physic-chemical characteristics (specific weight, pH, cationic exchange capacity, SB, V, Fe and Al extractable in oxalate, citrate-dithionite and pyrophosphate) and the chemical-mineralogical composition (parental material, clay minerals, silica, carbonates, iron oxides and oxy-hydroxides, heavy metals, organic compounds).

2. Grain-size distribution. For the determination of the grain-size distribution, the soil samples have been passed through a set of sized sieves, separating seven grain-size classes: < 0.010 mm; 0.010-0.020 mm; 0.020-0.100 mm; 0.100-0.200 mm; 0.200-1.000 mm; 1.000-2.000 mm and > 2.000 mm. The grain-size classes have been weighted using an analytical balance, and the obtained results have been reported to the total soil mass used for work [8, 19, 23].

3. Mineralogical analyses. For the determination of the mineralogical components from the studied soil samples was conducted a preliminary separation of the mineral fractions using heavy liquid and magnetic methods. The work procedures have been described in several previous studied [7, 10, 31]. The obtained mineral concentrated (83.50 ÷ 98.00 % monomineral) has been studied by X-ray diffraction (powder method, Phillips difractometer, CuK$_\alpha$ radiation), IR spectrometry (KBr pelted method, Bio-Rad IR spectrometer), differential thermal analysis (Netzsch thermal balance TG. 209 type) and optical microscopy (optic microscope MEYJ type, in natural and polarized light). For the clay minerals differentiation, the results of XRD analysis have been compared with the results of thermal analysis and IR absorption spectra [7, 10, 14, 22, 25, 31, 32, 41].

Table 1

The studied andosols

Sample	Deep, cm	Horizon	Observations
Profile MG.8 – Cambic Andosol			
MG.8-2628	9 - 5	Of	Localization: Gurghiu Mountains, under Bucin Pass, versant, slope 5-7^o, exposition E-SE. Altitudinal: 1200 m Parental material / underlying rock Andesitic weathering deposit / andesite
MG.8-2629	5 - 0	Oh	
MG.8-2630	0 - 15	Aou	
MG.8-2631	15 - 26	ABv	
MG.8-2632	26 - 41	Bv1	
MG.8-2634	60 - 80	BC+R	
Profile MG.16 – Cambic-histic Andosol			
MG.16-2100	14 - 0	Oh	Localization: Gurghiu Mountains, Borzonț Mountain, at cca 40 m on top, mountain plateau, slope 3-5^o, exposition N-NV Altitudinal: 1495 m Parental material / underlying rock andesitic weathering deposit / andesite with pyroxenes and amphiboles
MG.16-2101	0 - 5	Aou	
MG.16-2102	5 - 12	ABv	
MG.16-2103	12 - 32	Bv1	
MG.16-2104	32 - 54	Bv2	
MG.16-2107	54 - 70	Bv3	
MG.16-2108	70 - 90	BC+R	

4. The determination of the physical and chemical parameters. The specific weight was determined by picnometric method on samples with grain size < 0.020 mm, using benzene as dispersion liquid [19, 22, 31]. pH(NaF) and pH(H_2O) were obtained by potentiometric measurements using dispersion method (5 g soil / 50 mL 1 M NaF solution) [5, 9, 10, 39]. For the determination of ionic exchange capacity has been done two successive extractions with 1 M NH_4NO_3. In extract, the concentration of Ca, Mg, K and Na was determined by AAS in air-acetylene flame, and extractible Al and Fe by AAS in flame with high temperature (N_2O-C_2H_2). The effective ionic exchange capacity was determined by successive washing of soil samples with 0.01 M NH_4NO_3, followed by the extraction of adsorbed NH_4^+ ions with 1 M NaCl. The exchange acidity was obtained by potentiometric titration of extract in 1 M KCl with 0.1 M NaOH at pH = 7.8. The differentiation of Al and Fe reactive forms from soil was done by extraction with: (i) 0.2 M ammonia acid oxalate solution, at pH = 3 (4 hours at dark); (ii) 0.1 M sodium pyrophosphate solution, at pH = 10 (16 hours); (iii) 0.2 M sodium citrate – potassium dithionite solution (2 hours) [4, 19, 22, 25, 31, 39, 40].

5. The extraction and fractionation of soluble organic compound. The extraction and fractionation of soluble organic compound was done by liquid chromatography, using a silica column (10 grams; 70÷320 mesh) inactivated with n-hexane. The soil samples (1-3 g) have been used for extraction with dichloride-methane / methanol % (v / v): 1x25 mL, 3x15 mL. The extracts were passed by chromatographic column, and then by successive elution have been separated 4 organic fractions: elution with n-hexane (20 mL) – hydrocarbons and organic compounds with sulphur; elution with n-hexane / toluene (4:1; 30 mL) – ceridic and stereolitic esters and ethers; elution with n-hexane / ethyl acetate (35:2; 30 mL) – alkenolics compounds; elution with hexane / ethyl acetate (4:1; 30 mL) – n-alcohols, n-acids, steolitic alcohols, etc. The qualitative and quantitative analysis of organic compounds from extracted fraction was done by gas chromatography (GC-FID), with a Hewlett-Packard 5972 chromatograph [29, 31, 33, 38].

6. Humus determination. From the soil samples (cca 1.5 g) first were eliminated the other organic compounds (cerides, rezines, soluble organic compounds, etc.) by successive extraction with toluene, ethylic alcohol (95 %) and 1:1 toluene and ethylic alcohol mixture (10 mL solvent for each extraction). The separated solid phase, after washing with pure methanol and drying at 50°C, was refluxed with 50 mL 2 % HCl aqueous solution for 1 hour. The residual solid substance was separated by filtration, washed with pure methanol, dried at 50°C and used for extraction (0.1 M $Na_2P_2O_7$ and 0.1 M NaOH mixture; pH = 13). The extract was centrifuged for 30 min. at 7000 rpm. From the extract the humus was determined by potentiometric titration [19, 22, 31, 36].

RESULTS AND DISCUSSION

The andosols from Gurghiu Mts. are met in the altitudinal span between 1000 and 1600 m (very rarely higher), that represents 48.83 % of the whole surface. From the total soil cover, this soil type represents about 36.6 % (659.35 km^2), forming the most compact area of andosols occurrence from Romania. At the subtype level a large variety is observed (with multiple simple and double subtypes), while at the level of the percentage detained by each dominant remain the Haplic and Skeleti-haplic Andosols. From a pedogenetic view point, the allophanic andosols (specific mainly for the piroclastic plateaus) are subordinated to the non-allophanic ones. The parental materials for the reference profiles are represented by different thickness andesitic or pyroxenic weathering deposits, situated on different varieties of andesites (*tabs. 1, 3*).

Table 2

The grain-size distribution

Profile	MG.8		MG.16	
Grain-size class, mm	Limits	Average	Limits	Average
< 0.010	0.87-2.40	1.30	2.09-7.03	4.61
0.010-0.020	0.49-2.65	1.37	2.16-7.83	3.81
0.020-0.100	0.88-5.71	2.86	2.86-7.59	5.99
0.100-0.200	3.19-16.52	9.60	8.09-12.28	9.95
0.200-1.000	35.46-52.38	40.71	22.68-30.02	27.04
1.000-2.000	10.21-24.82	16.08	11.77-21.69	17.40
> 2.000	19.13-32.45	27.21	27.65-33.88	28.72

The grain-size analysis indicates the fact that the percentage of the grain-size classes in the andosol samples from the studied profiles varies in relatively large limits (*tab. 2, fig. 1*), in both profiles dominant are the fractions 0.200-1.00 mm, > 2.00 mm and 1.000-2.000 mm. For all the samples from these two profiles, in the grain-size classes distribution diagrams is visible the existence of two maximums, the first corresponding to the grain-size class of 1.000÷0.200 mm and the second to the > 2.000 mm grain-size class (skeleton) (*fig. 3 a*). This situation indicates the fact that the parent material of the studied andosols might come from two mineralogic-petrographical sources, represented by the piroclastes (volcanic ash and glass) and by andesitic rocks.

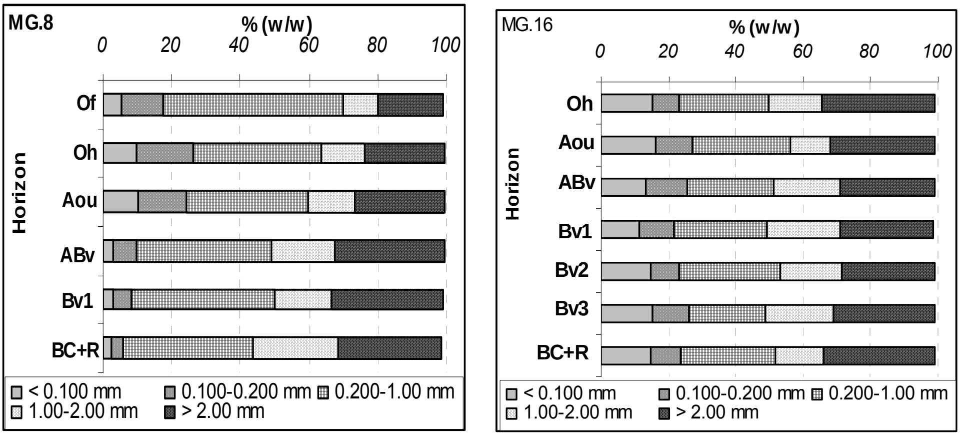


Figure 1. **The distribution of the grain size classes in the studied andosols**

Having in view the dimension of the particles and their percentages, we may appreciate that the parent materials from the studied andosols have a moderate-weak sorting degree, that indicates the fact that the studied perimeters are proximal-placed in relation to the source of petrographico-mineralogical material. The reduced rounding degree of the grains indicates their transportation on short distances, most probable by slow slope mass movement or / and by wind.

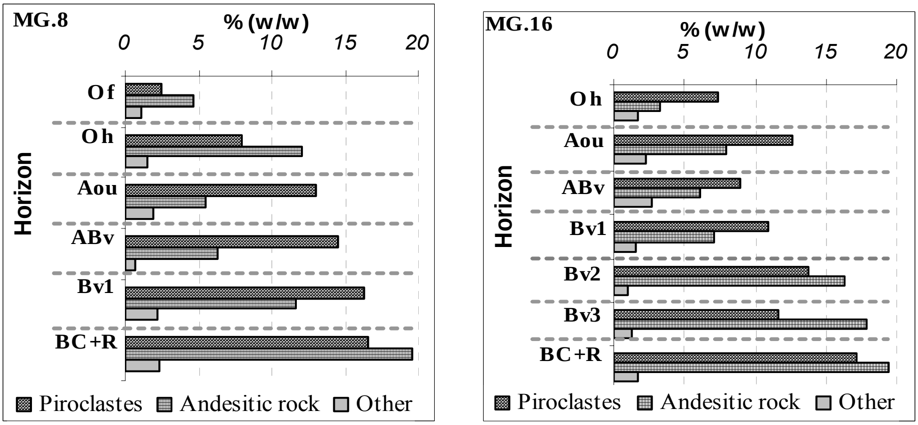


Figure 2. **The percentages of inorganic parental material in horizons of studied profiles**

The proportion of inorganic parental material varied between 8.31-38.51 % (media: 23.43 %) in MG.8 and 12.31-38.21 % (average: 24.65 %) in MG.16. From diversity point of view, the inorganic parental material from the two profiles is relative varied, being represented by: (i) piroclastes materials – ash and andesitic volcanic glass; (ii) fragments of andesitic rocks; (iii) secondary parental material – fragments of metamorphic and sedimentary rocks from source arias and those adjacent of studied perimeters. From the viewpoint of the percentage and importance in the soil genesis processes, the parent materials of andesitic and piroclastic nature are dominant and essential.

Table 3

The mineral and organic constituents of the studied andosols

Profile		MG.8		MG.16	
Specifications		Limits	Average	Limits	Average
Parental material	Piroclastes (1)	2.47-16.57	11.80	7.32-17.10	11.75
	Andesitic rock (2)	4.68-19.56	9.96	3.31-19.39	11.16
	Other components(3)	0.67-2.37	1.64	1.02-2.71	1.74
	Total	8.31-38.51	23.43	12.31-38.21	24.65
Clay minerals	Amorphous(4)	6.03-16.15	11.33	9.15-14.19	11.91
	Kaolinite	3.61-10.80	7.39	7.64-14.00	10.49
	Smectite(5)	0.68-1.94	1.06	0.71-2.77	1.67
	Illite(6)	0.68-1.94	1.06	1.16-3.22	1.99
	Others(7)	0.06-0.47	0.23	0.24-0.48	0.38
	Sum	10.79-27.90	21.11	22.60-28.76	26.37
Silica	Quartz	0.37-2.35	1.11	0.83-2.09	1.53
	Amorphous	1.33-3.03	2.40	1.92-3.35	3.07
	Total	1.75-5.05	3.56	3.36-6.15	4.69
Carbonates(8)		0,70-3.82	2.64	0.41-5.54	2.29
Fe-Ox(9)		1.15-3.15	2.12	1.97-5.09	3.24
Other minerals(10)		0.86-2.58	1.84	1.29-2.96	2.02
Organic compounds	Humus	12.07-23.14	17.37	12.45-25.82	19.62
	Other compounds(11)	1.10-2.11	1.66	0.04-5.35	1.96
	Total	13.85-25.53	19.23	12.45-28.50	21.72

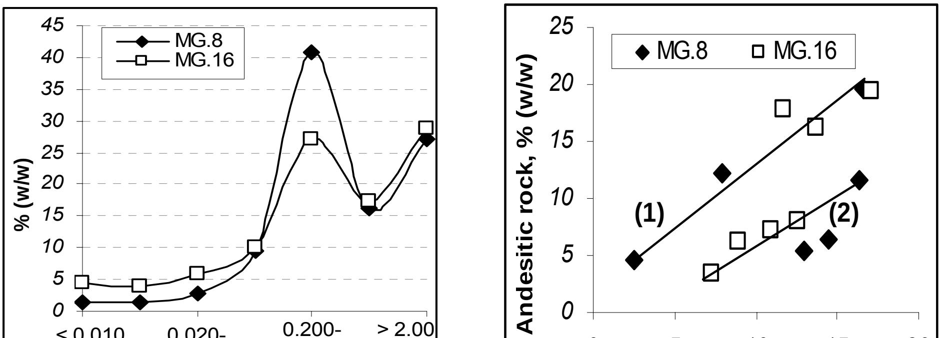
(1) Ash and volcanic glass – chemical composition and microscopic characteristics correspond to pyroxenic andesites (MG.8) and to pyroxenic andesites with amphiboles (MG.16). (2) Andesitic rock fragments. (3) Fragments of quartzitic and sericitous-chlorite schists, shales, sandstone, dolomite, apatite. (4) Allophane and imogolite.(5) Montmorillonite and subordinate vermiculite (incert lines in RX spectra). (6) Illite and subordinate hydromuscovite. (7) Halloysit, metahalloysit. (8)Calcite ($CaCO_3$) and subordinate: manganese calcite $(Ca, Mg)CO_3$; amorphous basic carbonates which contain Fe(II), Fe(II) and several minor elements (Ba, Sr, Pb, Cd, Co, Cr etc.). (9)Ferrihydrite, goethite, hematite. (10)K-feldspar, plagioclase feldspar, pyroxenes, garnets, muscovite, hornblende, biotite, amphiboles, anatase, ilmenite, magnetite ş.a. (11)Mono- and polysaccharides (mannose, galactoze, xyloze, arabioze); superior aliphatic hydroxi-acids and aromatic hydroxiacids; alcohols and superior aliphatic and aromatic polyols; sterols; aminoacids and polypeptides. The difference until at 100 % is determined by the vegetal material in incipient decomposition stages (was not considered in average samples formation) and the water soluble extract.

The variation of grain-size fractions proportions in these two profiles (*tab. 2*), the distribution of grain-size fractions in studied profiles (*fig. 1*), and the correlations between the piroclastes proportion and the proportion of andesitic rock fragments (*fig. 3 b*) indicate an accentuate modification of mineralogy and chemistry at superior horizon level: Aou (profile MG.8), Aou and ABv (profile MG.16). This variation can be interpreted as a consequence to the time modification of pedogenesis conditions (*tab. 4*), which are reflected in particular evolution of the andosolization process.

Table 4

The physic-chemical characteristics of studied andosols.

Profile		MG.8		MG.16	
Specifications		Limits	Average	Limits	Average
Specific weight, g.cm^{-3}		0.33-0.68	0.4683	0.42-0.81	0.55
pH	H_2O	4.58-6.23	5.41	5.20-6.19	5.70
	NaF	9.61-11.39	10.40	9.77-11.69	10.67
Ionic exchange capacity, mEchiv. / 100 g soil	Na^+	0.17-1.34	0.62	0.18-0.98	0.43
	K^+	0.41-2.11	1.17	0.63-1.49	1.09
	Ca^{2+}	1.03-2.89	2.05	1.05-3.38	2.15
	Mg^{2+}	0.34-2.37	1.44	0.25-2.09	1.08
	H^+	68.93-87.88	79.35	76.85-86.19	81.01
	T	75.69-90.04	84.03	80.37-91.33	85.78
SB, mEchiv. / 100 g soil		2.16-8.71	5.29	2.52-7.17	4.76
V, %		2.40-10.72	6.44	3.03-8.12	5.52
Fe extractable, %	Oxalate acid	0.77-2.20	1.42	0.95-2.15	1.44
	Citrate – dithionite	0.85-2.78	1.79	1.66-2.61	2.06
	Pyrophosphate	0.57-1.29	0.88	0.38-1.53	0.91
Al extractable, %	Oxalate acid	0.75-3.31	2.03	1.14-3.52	2.31
	Citrate – dithionite	0.63-3.09	2.10	1.55-4.05	2.77
	Pyrophosphate	0.47-2.11	1.44	0.79-2.73	1.84
Exchangeable Al, mEchiv./100 g		2.10-4.57	3.39	1.87-4.68	2.45

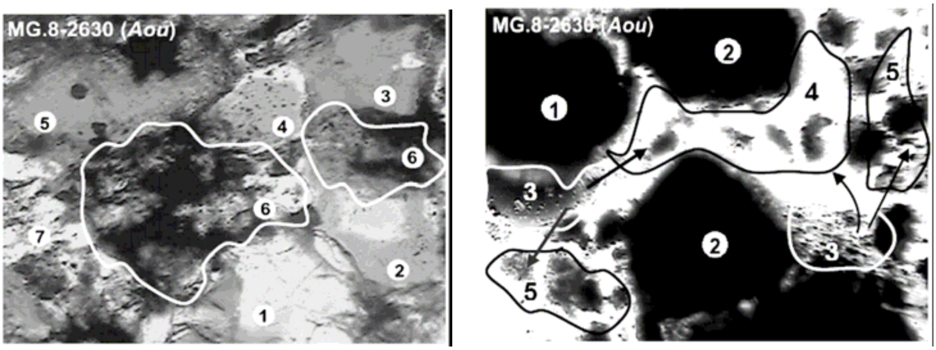


a. b.

Figure 3. **(a) The cumulative grain-size distribution for studied andosols (average values on profile). (b) The correlations between piroclastes and andesitic rock in studied andosols**

The anterior observations, correlated with the field surveys and the laboratory investigations, lead to the conclusion that the genesis of the studied andosols could be realized in two stages: (i) in the first stage the andosolization occurred mainly on the background of the andesitic rocks, the initial andosols having a non-allophanic character; (ii) in the second stage, over the initial andesitic rocks have been laid down volcanic ashes and glass (also of andesitic nature, that most probably came from the eruptions of the last eruptive cycle from the region - *Pannonian*), the andosols formed on piroclastic materials demonstrating a pronounced allophanic character.

The andesitic rock, on the basis of chemical composition and microscopic characteristics correspond to the pyroxenic andesites (MG.8) and to pyroxenic andesites with amphiboles (MG.16). The percentages of andesitic rock fragments varied between 4.68-19.56 % (average: 19.96 %) in MG.8 and between 3.31-19.30 % (average: 11.16 %) in MG.16, these being concentrated predominant in 1.00-2.00 mm and > 2.00 mm grain-size fractions (*tab. 3, fig. 2*).



a. b.

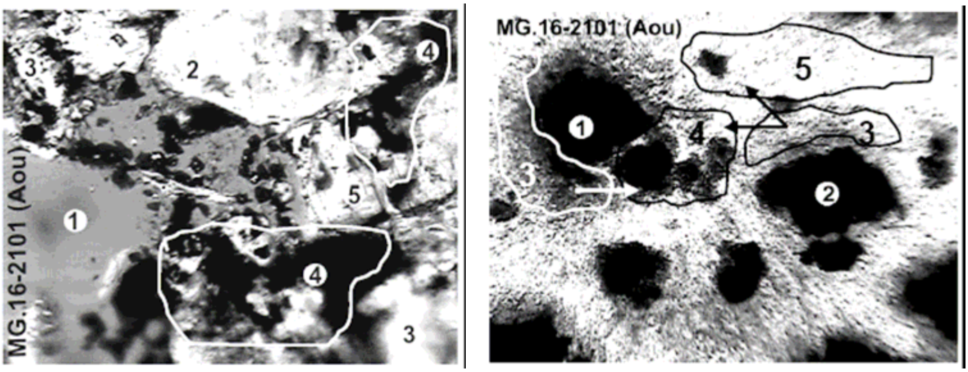
Figure 4. **The andosol sample MG.8-2630 (Aou): (a) microscopic image in thin layer, enlargement: 400x:** (1) quartz, (2) feldspars, (3) pyroxene (enstatite-hyperstene), (4) and (5) weathered volcanic glass granules, (6) allofano-humus complex, (7) clay minerals (kaolinite associated with amorphous silica). **(b) The allophane formation (microscopic image in thin layer, enlargement: 500x):** (1) and (2) volcanic glass granules having as main weathering tendency the formation of allophane I – zone 3 (aluminous, probably imogolite) and / or of allophane II (silicious) – zona 4. The allophane I is transformed, in time, in allophane II or / and kaolinite– zone 5.

The piroclastic material, from the mineralogical-petrographic view point, correspond to the andesites, but the chemical composition of these is sensible different towards of andesitic rock fragments. This may be due both, to different origins, or to different weathering degree of piroclastes and andesitic rock fragments. Our results indicate that the firs hypothesis is more probable. The percentages of piroclastic material varied between 2.47-16.57 % (average: 11.80 %) in MG.8 and 7.32-17.10 % (average: 11.75 %) in MG.16, these being predominant concentrated in 0.100-0.200 mm and 0.200-1.000 mm grain-size fractions (*tab. 3, fig. 2*).

The secondary parental material is represented by fragments of quartzitic and sericitous-chlorite schists, shales, sandstone, dolomite, etc., K- and plagioclase feldspars, pyroxenes, garnets, muscovite, hornblende, biotite, amphiboles, ilmenite, etc, respectively. Their percentages varied between 0.67-2.37 % (average: 1.64 %) in MG.8 and 1.02-2.71 (average: 1.64 %) in MG.16 (*tab. 3, fig. 2*).

The frequent occurrence form of the piroclastes in the studied andosols (from our estimations > 90 %) is that of grains associated with the other mineral and organic components. The microscopic studies, IR spectrometry, DRX and chemical analyses (*fig. 4, 5*), have shown that the piroclastes may form both macroscopic (agglomerates) and microscopic (with a colloidal character – macro-micelles) associations.

The macroscopic piroclastic associations (agglomerates) have a higher occurrence frequency and are characteristic to the > 2.00 mm and 2.00-1.00 mm grain-size classes. They may have dimensions of 1.00-37.00 mm, dominant as percentage in the andosols being the agglomerates with dimensions of 1.00-3.00 mm. The agglomerates of < 3.00 mm dimensions are characteristic to the upper and lower horizons: Of, Oh, Bv1, BC+R (MG.8), Oh, Aou, Bv3, BC+R (MG.16). The agglomerates of > 3.00 mm have a higher occurrence frequency in the middle horizons: Aou, ABv (MG.8), ABv, Bv1, Bv2 (MG.16), respectively.



a. b.

Figure 5. **The andosol sample MG.16-2101 (Aou): (a) microscopic image in thin layer, enlargement: 400x**: (1) granule of weathered volcanic glass, (2) feldspars, (3) clay minerals (kaolinite associated with amorphous silica), (4) allofano-humus complex, (5) quartz. **(b) The allophane formation (microscopic image in thin layer, enlargement: 500x)**: (1) and (2) volcanic glass granules having as main weathering tendency the formation of allophane I – zone 3 (aluminous, probably imogolite) and / or of crystalline clay minerals (kaolinite) – zona 4. The allophane I is transformed, in time, in allophane II (zone 5) or / and kaolinite

According to the nature, quantitative ratio and distribution mode of the components, in the studied andosols have been described two main types of piroclastic macroscopic associations: (i) *agglomerates with clayey cement*; (ii) *agglomerates with aluminosilicatic cement*. These occur in all the horizons of the studied profiles, with morphologic, structural and composition differentiations from a profile to another and between the horizons of the same profile. Qualitatively, on a profile may be appreciated a relative decrease of the agglomerates with clayey cement (these being characteristic to the upper horizons: Of, Oh, Aou – MG.8; Oh, Aou, ABv, Bv1 – MG.16) and a relative increase of the proportion of those with aluminosilicatic cement (characteristic to the lower horizons: Bv1, BC+R în MG.8; Bv2, BC+R in MG.16.

The piroclastic agglomerates with clayey cement are more friable; have in their interior numerous spaces, cracks and channels filled with iron oxy-hydroxides (amorphous), organic matter, amorphous silica or carbonates depositions. The distribution of the components in these agglomerates does not have a specific character. The cement is mainly clayey (allophane and kaolinite in fine dispersed state), has an aspect of amorphous mass and includes strata-like, lenses or oolitic accumulations of iron oxy-hydroxides (amorphous; may yet appear and in fine dispersed state pigmenting the amorphous mass of the cement), amorphous silica, carbonates and organic matter.

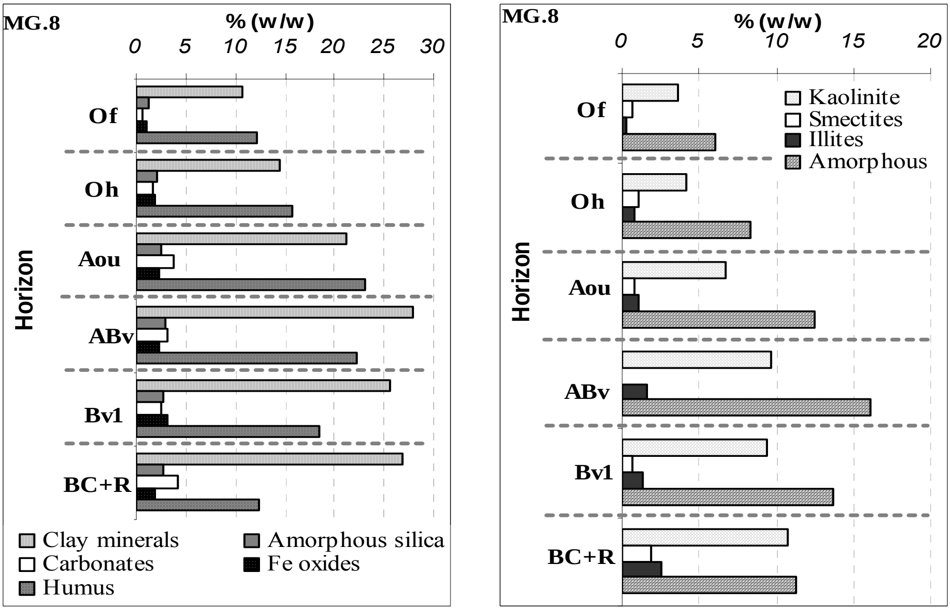


Figure 6. **The percentages of mineral and organic components in horizons of MG.8 profile**

The piroclastic agglomerates with aluminosilicatic cement have a higher hardness than the clayey-cemented ones (are dispersed only after intense trituration). They have a compact, heterogeneous aspect, the internal spaces and cracks are more reduced as percentage, being filled with clayey minerals (allophane, kaolinite, subordinately illite), iron oxy-hydroxides (ferrihydrite) and with variable quantities of organic matter. The cement is formed of aluminosilicatic gel (in different stages of geochemical differentiation) with aspect of an amorphous mass, associated with variable quantities of clay minerals (allophane, kaolinite) in fine dispersed state, organic matter, subordinate quantities of amorphous iron oxy-hydroxides and carbonates. Locally, in the amorphous aluminosilicatic mass appear strata-like, lenses or oolitic accumulations of iron oxihydroxides, carbonates, clay minerals, amorphous silica (associated with variable quantities of organic matter).

The colloidal associations of macro-mycelar character appear in all the horizons of the studied profiles, being differentiated as composition and structure (*figs. 4, 5*). Their major components are the amorphous clay minerals (allophane, imogolite), humus and variable quantities (according to the nature of the parent material and the horizons they are met in) of kaolinite, iron oxy-hydroxides (ferrihydrite), amorphous silica and carbonates. According to our estimations based on the chemical analyses, microscopic and IR spectrometry studies, over 80% of the amorphous clay minerals (imogolite, allophane) and of the humus are included in allophano-humic complexes.

Between inorganic components of andosols, the clay minerals are quantitatively dominant, these being represented by: (i) amorphous clay minerals: allophane, imogolite, proto-imogolite; (ii) kaolinite; (iii) smectite – Ca-Na morthmorillonite; (iv) illite and hydromuscovite; (v) halloysite and metahalloysite (*tab. 3*, *figs. 6, 7*). The mineralogy and chemistry of studied andosols are dominated by allophanes, the quantitative ratio of these representing and a differentiation criteria between allophonic and non-allophanic types.

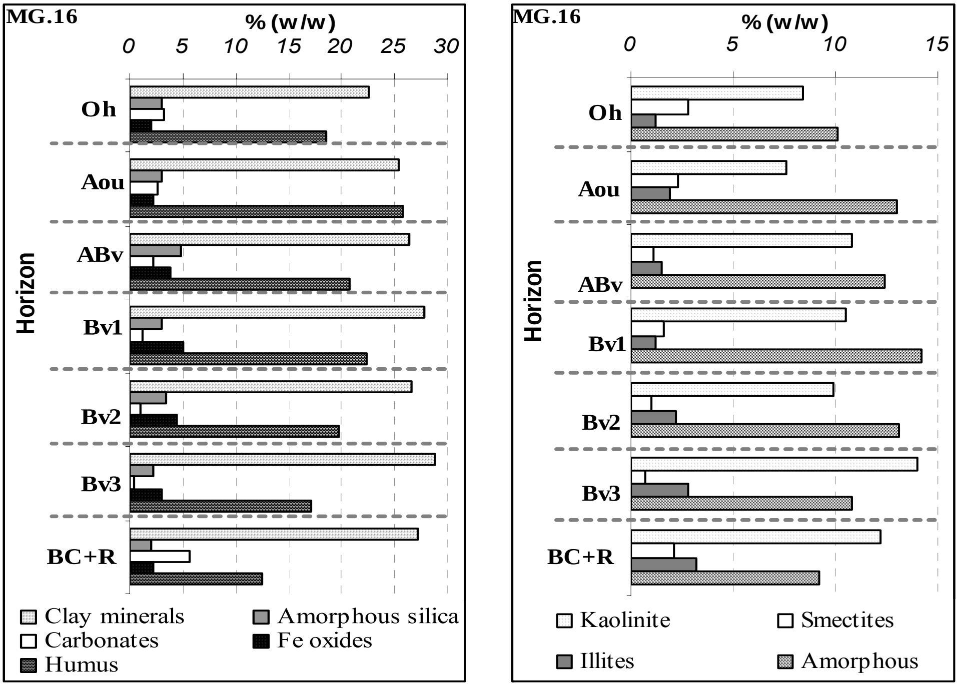


Figure 7. **The percentages of mineral and organic components in horizons of MG.16 profile**.

The clay minerals are exclusive by authigene nature and have a percentages between 10.79-27.90 % (average: 21.11 %) in MG.8 profile and between 22.60-

28.76 % (average: 26.37 %) in MG.16 profile (*tab.3, figs. 6, 7*). The type, proportion and occurrence way of clay minerals are evident correlated with weathering processes of piroclastic material and of andesitic rock granules.

The clay minerals can be in the composition of agglomerates cement (being always associated with variable quantities of organic compounds, alunimo-silicated gel, iron oxy-hydroxides and carbonates) and / or in composition of pellicles deposed by agglomerated surface. The microscopic studies and physic-chemical analyses have indicated some correlations between agglomerates characteristics and the cement components ratio, and the occurrence horizons, respectively.

The kaolinite appears frequently as compact white-yellow masses, formed from granular and lamellar aggregates. Towards others clay minerals, he is better crystallized and associated almost all the time, with subordinated and variable quantities of montmorillonite and halloysite.

The amorphous clay minerals are represented by allophane, imogolite and possible protoimogolite; have authigene origin and are directly correlated with the weathering stages of piroclastic material and andesitic rock granules. According with ours estimations, over 80 % from amorphous clay minerals appear associated with humus and kaolinits, as macromicelles. The structure and the ratio between the components of allphano-humic complexes varied as a function of the allophanic or non-allophanic character of andosols. The association allophane – kaolinite ± (imogolite, halloysite, metahalloysite) represent one of the main paragenesis used for the differentiation of andosols types and for elucidation of those formation.

In studied andosols, allophane appears in two forms: (i) allophane I (aluminous, possibly protoimogolite or imogolite) with the chemical formula $(Al_2O_3)_{1,053}(SiO_2)_{1,449}(H_2O)_{2,683}$ and (ii) allophane II (siliceous) with the formula $(Al_2O_3)_{1,108}(SiO_2)_{1,907}(H_2O)_{3,160}$. Allophane I appear especially in the non-allophanic andosols, while allophane II is characteristic to the allophanic andosols. The observation is concordant with the variation tendencies on the profile of the allophane / kaolinite ratio, respectively the pyrophosphate-extractible Al / oxalate-extractible Al ratio (*tabs. 3, 4*). In the conditions of the studied andosols, there is an dynamic equilibrium between the two allophane forms, conditioned by pH, the content of organic matter and the thermodynamic activity of Al, Si and Fe. From our calculations, reported to the conditions of the studied andosols, for an average content of soil organic carbon of about 12 %, the limits of the stability domains for allophane I are $a_{SiO_2} / a_{Al_2O_3} = 0.3 - 1.0$, and for allophane $a_{SiO_2} / a_{Al_2O_3} = 2.5 - 4.5$. The variation of the soil organic matter content may determine the confinement or enlargement of these domains.

We observed that the varieties of allophane with a small content of aluminum (named by us allophane I, possibly protoimogolite or imogolite) are progressively transformed in an allophane variety richer in silica (named allophane II), process accompanied by the retention in the allophano-humic complexes of significant quantities of organic matter. The high quantities of organic matter retained in the horizons of the studied profiles are explained by the protective action manifested by allophane [1]. According to a series of studies [28, 34, 35], at small pH values (pH < 5) organic matter may also manifest an anti-allophanic effect, translated into the destabilization of the allophano-humic associations, with the formation of the metal (Al, Si)-humus complexes. From these complexes, Al is the hardest levigated substance, restrictively participating to the reactions of polycondensation with the soluble silica [6], fact that inhibits the precipitation of allophane. In the case of the studied andosols, the anti-allophanic effect is relatively intense manifests and with a rhythmic character, depending on the precipitation regime, the nature of the parent material and the physical and chemical characteristics of the soil solution.

CONCLUSIONS

1. In Gurghiu Mountains the andosols represent about 36.6 % (659.35 km^2) from the total soil cover, forming the most compact area of andosols occurrence from Romania. At the subtype level dominant are Haplic and Skeleti-haplic andosols, and at the pedogenetic level, the allophanic andosols (specific to piroclastic plateaus) is subordinated to the non-allophanic andosols.

2. The parental materials are mainly of a vitroclastic character and come from two different petrographic-mineralogic sources, represented by piroclastes (volcanic ash and glass) and andesitic rocks. They have a moderate-weak sorting degree, and the transport of the parent material was realized on short distances, most probable by slow slope mass movement or / and by wind. From a chemical and mineralogical viewpoint the parent material corresponds to pyroxenic andesites (profile MG.8) and to pyroxenic andesites with amphiboles (profile MG.16).

3. The mineralogy and chemistry of studied andosols are dominated by allophane and kaolinite, their quantitative ratio representing differentiation criteria between allophanic and non-allophanic types. According with ours estimations, over 80% from amorphous clay minerals and from humus are included in allophano-humic associations. The structure and the ratio between the components of allphano-humic complexes varied as a function of the allophanic or non-allophanic character of andosols.

4. The allophane appears in two forms: (i) allophane I (aluminous, possibly protoimogolite or imogolite), characteristic to the non-allophanic andosols, and (ii) allophane II (siliceous), characteristic to the allophanic andosols. Between the two allophane forms is an dynamic equilibrium between conditioned by pH, the content of organic matter and the thermodynamic activity of Al, Si and Fe.

5. The genesis of the studied andosols was most probably realized in two stages: (i) in the first stage the andosolization occurred mainly on the background of the andesitic rocks, the initial andosols having a non-allophanic character; (ii) in the second stage, over the initial andesitic rocks have been laid down volcanic ashes and glass (also of andesitic nature, that most probably came from the eruptions of the last eruptive cycle from the region - Pannonian), the andosols formed on piroclastic materials demonstrating a pronounced allophanic character.

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