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GEOCHEMICAL ASPECTS OF THE MOHOȘ PEATLAND FROM HARGHITA MOUNTAINS

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Abstract: Geochemical analysis of samples peat bog collected from Mohoș area to allow determination of potential pollution sources. The elemental analysis shows a high content in carbon and a low content in oxygen and nitrogen. The pH lower, from 3.18 to 4.77, with low ash content, indicates us a low degree of decomposition of peat samples. The mineral assemblage found from XRD analyses of peat samples shows the presence of the following minerals: quartz, followed by clay minerals, feldspars, and minerals associated with the presence of organic matter. Additionally, the samples contain iron and titanium oxides such as hematite, goethite and rutile. For elemental analysis CHNS-O was used a EuroEa 3000 EuroVector and for examination of the mineralogy of peat samples was used X-ray diffraction.

Keywords: ombrotrophic bog, Mohoș, TOC, X-ray diffraction, pH, redox potential

1. INTRODUCTION

Peat covers approximately 4 % of the land area of the world, and 95 % of this peatland is in the cold and temperate zones from the northern hemisphere (Deboucha et al., 2008). One third of European peatlands are present in Finland, in Romania the peatland are distributed on the 39 km^2 (Montanarella et al., 2006).

Peat deposits are formed when organic matter accumulates more rapidly than it decays over thousands of years. The microbial degradation of plant residues is regarded as a result of poor aeration and acidic conditions below a high water table. The peat deposit often consists of more than 75 % organic substances (Andriesse, 1988).

Ash remaining after the burning of peat at 550° C is important in the characterization of peatland type. In ombrotrophic bogs, ash contents that reflect atmospheric-dust deposition are generally very low, between 1 and 3 % (Steinman and Shotyk, 1997). The mineral composition of ombrotrophic peat is homogeneous with depth. The ombrotrophic peat contains mainly quartz (60-90 %) and opaline silica (30-70 %) with less amounts of feldspar (5-15 %) and muscovite (5-15 %) (Steinmann and Shotyk, 1997).

The aim of the present paper is to describe the structural properties of peat samples which were collected from Mohoș peatland located in the southern part of Harghita Mountains, in Ciomadul crater, using the analysis of physic-chemical parameters, organic matter content, elemental analysis (CHNS-O) and X-ray diffraction, using the powder method.

2. GEOLOGICAL FRAMEWORK

With its over 160 km length, the Călimani-Gurghiu-Harghita (CGH) chain is the longest continuous volcanic range in the Carpatho-Pannonian Region. The Harghita Mountains represent the largest and most complex volcanic structure at the southern part of the CGH range in Romania, Neogen/Quaternary andesite and dacite (Szakács and Seghedi, 1995).

The Ciomadul is the main chain-ending volcano in the South of the Harghita Mountains, which is the southern segment of the CGH volcanic range in the East Carpathians, Romania (Fig. 1) (Szakács et al., 2015) and is composed of about 8-14 km^3 dacitic eruptives (Karátson and Timár, 2005; Szakács et al., 2015). The Ciomadul is the youngest volcano of the Carpathian–Pannonian region, which erupted last time at 32 ka. It produced high-K dacitic lava domes and pumiceous pyroclastic rocks. The dacite contains plagioclase, amphibole in addition to biotite, titanite, apatite, zircon and occasionally quartz, K-feldspar, olivine, clinopyroxene and orthopyroxene (Harangi et al., 2015).

The Mohoș peatland formed in the northern crater of Ciomadul massif, at an altitude of 1050 m in Harghita Mountains. The depth of the Mohoș caldera is estimated to be approximately 60 m, but his value is constantly changing due to sedimentation processes that take place (Diaconu and Mailat, 2007).

3. MATERIALS AND METHODS

The studied peat samples were collected from Mohoș peatland in August 2015, up to 30 cm deep under vegetation cover (Fig. 1), dried in an electric oven at 50° C and sieved at 0.63 mm. Redox and pH measurements were determined on all 50 samples, used an portable kit HACH HQ 40d. Ash content was determined by burning the peat samples at 550° C for 4 h expressing the results as percentage of the dry weight of the samples.

For elemental geochemical analysis was used a EuroEa 3000 EuroVector elemental analyzer to measure % TOC, H, N, S and O from Department of Geology, "Al. I. Cuza" University, Iaşi. Samples were crushed, followed by a 4 N HCl treatment for 24 h to remove inorganic carbon. The remaining material was washed with distilled water several times to remove the acid, and then dried at 50° C (Ortiz and Gentzis, 2015).

For the X-ray diffraction analyses, the samples were homogenized manually in an agate mortar to obtain the optimum particle size and to ensure the random orientations of the crystals in the samples (Tyni et al., 2014). XRD measurements were performed on representative powdered peat samples using a Shimadzu LabX XRD-6000 diffractometer (Cu Kα radiation λ = 1.5406Å), operating at 40 KV, with a beam current of 30 mA. Scans were recorded from 5 to 80º 2θ, with a scan steed of 1 deg/min and a sampling pitch of 0.02 deg.

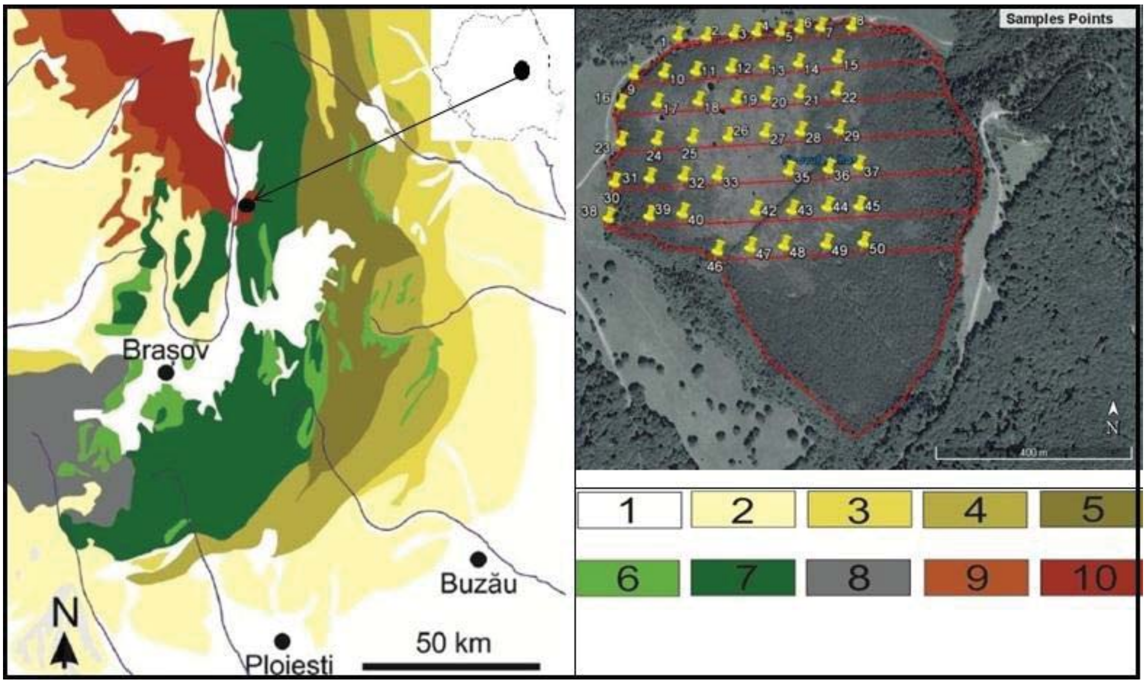

Fig. 1. Geological map and the samples points: 1 – Quaternary, 2 - Pannonian-Sarmatian, 3 - Paleozoic, 4 - Paleocene-Miocene, 5 - Oligocene, 6 - Neocomian, 7 - Tithonian-neocomian, 8 - Paleogene, 9 - Vucanogene Neogene deposits, 10 - Neogene volcanic (after Frunzeti, 2013)

4. RESULTS

Since the peat samples containing between 80-98% organic matter, pH is acidic, from 3.18 to 4.7 and the redox potential from 135.2 to 225.4 mV, Mohoş peatland can be classified as a ombrotrophic peatland. The degree of decomposition, according to von Post humification test, is between H1-H3 with high fiber content, partially decomposed, in brown colored.

The elemental composition, atomic ratios (H/C and C/N) of the studied peat samples are shown in Table 1. Because of the absence of carbonates, total carbon was assumed to be Total Organic Carbon (TOC) (Delarue et al., 2011). From the samples which were analysed, T_1 had higher percentages of carbon (46.09 %) and nitrogen (2.50 %), while T_{29} had a greater concentration in hydrogen (5.37 %) and T_{29} in oxygen (54.61 %). The H/C ratio is indicators for the percentage saturation of the C atoms within the organic molecule and of the carbohydrate content respectively. Lower H/C ratios indicate higher aromaticity in the samples (Fernandes et al., 2012).

The C/N ratio has been considered an index of the possible microbial activity because these communities need at least a C/N ratio of 30 to carry out the organic material decomposition. A decrease C/N ratio below 30 shows the increased of rate decomposition of organic matter (Kuhry and Vitt, 1996). C/N ratio confirms that the samples analyzed shows a close decomposition rate. The data in Table 1 confirm that the T_{12} sample is more decomposed, the nitrogen enrichment in T_{12} being related to a greater incidence of microorganisms, including bacteria, fungi, and actinomycetes, at this stage of decomposition

(Kuhry and Vitt, 1996). Another reason for which samples T_{12} and T_1 are more decomposed is that they were under incidence of water.

Table 1. Samples with the highest content in CHHS-O and atomic ratios.

Sample	N (%)	C (%)	H (%)	S (%)	O (%)[a]	H/C[b]	C/N[c]
T_{29}	2.09	44.43	5.37	0	48.09	1.44	24.71
T_{12}	2.12	38.43	4.82	0	54.61	1.49	21.13
T_1	2.50	46.09	5.25	0	46.14	1.35	21.45

[a]By difference of mean values.
[b]H/C=[(%H/1.008) / (%C/12.01)].
[c]C/N=[(%C/12.01) / (%N/14.00)].

Detailed examination of the mineralogy of the peat samples using XRD is shown in the Fig. 2a and Fig. 2b. The XRD diffractogram shows a hump, between 10° and 30°, highlight the amorphous matter that includes vitreous phases and gels (Tiainen et al., 2002). Analyzing the processes involved in peat formation, we recognized an anaerobic thick structural layer, which is formed of residual material from the original plant structure, decay products and new substances produced mainly by bacteria. At this level peat is amorphous and highly humified (Bozkurt et al., 2001).

Mineral phases consist of detrital minerals such as silicates, mainly quartz. They are followed by clay minerals (illite, kaolinite and dickite) and feldspar (anorthite and albite). There were small amounts of carbonates such as calcite and dolomite, and phosphate such as calcosiderite. It was observed the presence of the heavy minerals, dominated by iron and titanium oxides: hematite, goethite and rutile. Additionally, occurring minerals associated with the presence of organic matter (efremovite, simonellite) or coals (alunogen) and with the carbonification of wood (rorosite).

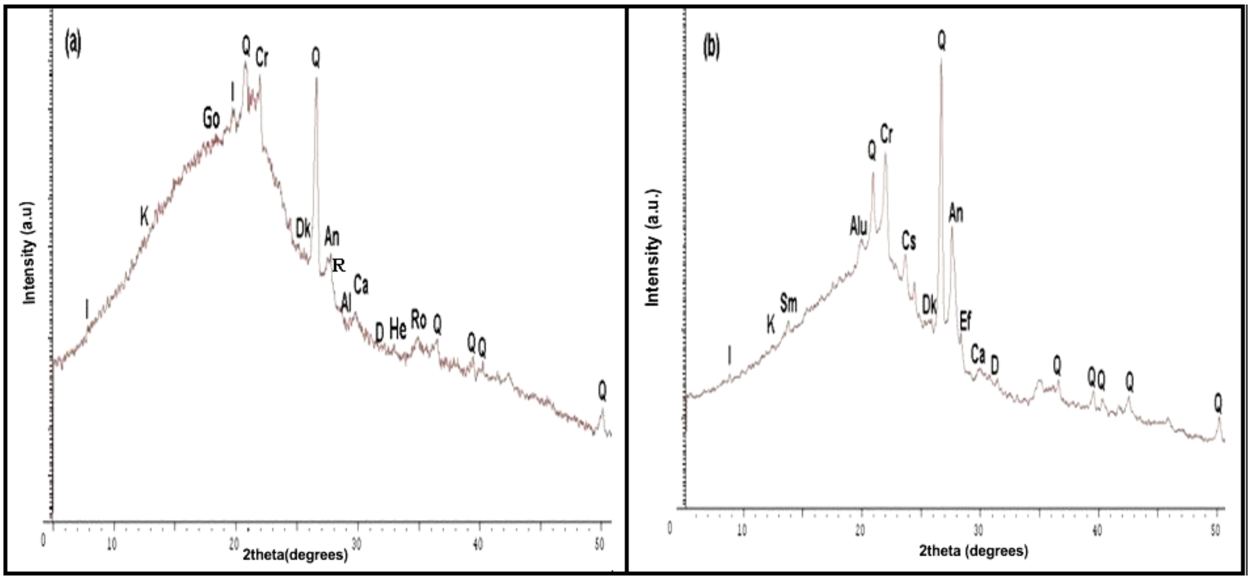

Fig. 2. XRD diffractograms of the peat samples (where Q=quartz, Cr=cristobalite, I=illite, K=kaolinite, Dk=dickite, An=anorthite , Al=albite, Ca=calcite, D=dolomite, Cs=calcosiderite, Ef=efremovite, Sm=simonellite, Ro=rorosite, Alu=alunogene, He=hematite, Go=goethite, R=rutile

5. CONCLUSIONS

The ombrotrophic nature of Mohoş peatland is given by low ash content, acid pH and low redox potential. The high content of organic material indicates the early stage of decomposition of plant materials due to the different areas of training and accumulation of inorganic materials, especially silicon dioxide, in the top layer of peat bogs.

The critical factors influencing the mineralogy of peatland are distance from pollution source and water conditions within the peatland. The minerals that dominate the inorganic fraction are detrital minerals such as quartz, clay and feldspars. The heavy minerals are represented by iron and titanium oxides: hematite, goethite and rutile. Mohoş peatland receive mineral particles from soil dust supplied by the atmosphere, resulting from the operation of quarries (andesites from Bixad, dolomite from Voşlobeni, kaolin in Harghita Bai or from Balan mine, followed by the construction of dumps close to it).

REFERENCES

Andriesse, J.P., 1988. Nature and management of tropical peat soils. 1st ed., FAO, Rome.

Bozkurt, S., Lucisano, M., Moreno, L., Neretnieks, I., 2001. Peat as a potential analogue for the long-term evolution in landfills. Rev. Earth-Sci., 53(1-2), p. 95-147.

Deboucha, S., Hashim, R., Alwi, A., 2008. Engineering properties of stabilized tropical peat soils. Electronic Journal of Geotechnical Engineering (EJGE), 13, Bundle E, p. 1-9.

Delarue, F., Laggoun-De´farge, F., Disnar, J.R., Lottier, H., Gogo, S., 2011. Organic matter sources and decay assessment in a Sphagnum-dominated peatland (Le Forbonnet, Jura Mountains, France): impact of moisture conditions. Biogeochemistry, 106, p. 39-52.

Diaconu, D.C., and Mailat, E., 2007. Complex study of lake ecosystems in the Mohoş Swamp. Faculty of Geography. University of Bucharest. Bucharest, Romania (in Romanian).

Fernandes, A.N., Girardello, F., Esteves, V.I., Sierra, M.M.D., Giovanela, M., 2012. Structure and properties of subtropical Brazilian peat samples. In Peat: Formation, Uses and Biological Effects. Nova Science Publishers: New York, p. 125-142.

Frunzeti, N., 2013. Geogenically emissions of greenhouse gas in the southern sector of the Eastern Carpathians (in Romanian). Ph.D. Thesis, "Babeş- Bolyai" University, Cluj-Napoca, Romania.

Harangi, S., Novák, A., Kiss, B., Seghedi, I., Lukács, R., Szarka, L., Wesztergom, V., Metwaly, M., Gribovszki, K., 2015. Combined magnetotelluric and petrologic constrains for the nature of the magma storage system beneath the Late Pleistocene Ciomadul volcano (SE Carpathians). Journal of Volcanology and Geothermal Research 290, p. 82-96.

Karátson, D., Telbisz, T., Harangi, S., Magyari, E., Dunkl, I., Kiss, B., Jánosi, C., Veres, D., Braun, M., Fodor, E., Biró, T., Kósik, S., von Eynatten, H., Lin, D., 2013. Morphometrical and geochronological constraints on the youngest eruptive activity in East-Central Europe at the Ciomadul (Csomád) lava dome complex, East Carpathians. J. Volcanol. Geotherm. 255, p. 43-56.

Karátson, D., and Timár, G., 2005. Comparative volumetric calculations of two segments of the Neogene/Quaternary volcanic chain using SRTM elevation data: implications for erosion and magma output rates. Z Geomorphol Suppl 140, p. 19-35.

Kuhry, P., and Vitt, D.H., 1996. Fossil C/N ratios as a measure of peat decomposition. Ecology 77, p. 271-275.

Montanarella, L., Jones, R.J.A., Hiederer, R., 2006. The distribution of peatland in Europe. Mires and Peat, Vol.1, p. 1-10.

Ortiz H.C., and Gentzis, T., 2015. Critical considerations when assessing hydrocarbon plays using Rock-Eval pyrolysis and organic petrology data: Data quality revisited. International Journal of Coal Geology 152, p. 113-122.

Steinmann, P., and Shotyk, W., 1997. Geochemistry, mineralogy and geochemical mass balance on major elements in two peat bog profiles (Jura Mountains, Switzerland). Chemical Geology, 138, p. 25-53.

Szakács, A., Seghedi, I., Pécskay, Z., Mirea, V., 2015. Eruptive history of a low-frequency and low-output rate Pleistocene volcano, Ciomadul, South Harghita Mts. Romania. Bull Volcanol, 77-12.

Szakacs, A., and Seghedi, I., 1995. The Călimani–Gurghiu–Harghita volcanic chain, East Carpathians, Romania: volcanological features. Acta Volcanol. 7, p. 145-155.

Tiainen, M., Daavitsainen, J., Laitinen, R.S., 2002. The role of amorphous material in ash on the agglomeration problems in FB boilers. A powder XRD and SEM-EDS study. Energy Fuels, 16(4), p. 871-877.

Tyni, S.K., Karppinen, J.A. Tiainen, M.S., Laitinen, R.S., 2014. Preparation and characterization of amorphous aluminosilicate polymers from ash formed in combustion of peat and wood mixtures. Journal of Non-Crystalline Solids 387, p. 94-100.