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IN DEPTH VARIATION OF WATER PROPERTIES FOR ST. ANA LAKE – ROMANIA RELATED TO SEDIMENTS IN SUSPENSION

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ABSTRACT. The minerals identified in the sand shore and mud from the bottom of St. Ana Lake is: biotite, potassic feldspar, hornblende, potassic muscovite, and hydrate silicate mixed with amorphous andesite. Such mineral particles were observed suspended in the water from an average depth of 2 m to the bottom. The suspended particle average diameter and density increases along with the water depth, which may affect water properties. We found that the electrical conductivity is close to the distilled water in the upper layers and increases to the bottom due to the dissolved mineral ions. The turbidity is very low, at the surface and progressively increases at 4 meter depth, because of the particle density variation in lower water layer. The pH has an acid range. The pH values are slowly decreasing with the water depth due to the acid pH of phylosilicates. The main metal found is Fe, the concentration is considerably below the standard limit. It increases with water depth due to the increased concentration of biotite and hornblende particles floating in the water. There were also identified traces of Zn and Cu in very low concentrations and no traces of Pb and Cd. All measurements performed in July 2010 prove that the St. Ana Lake presents a normal state for a closed water system with no pollution trace.

Keywords: *volcanic lake, turbidity, electrical conductivity, pH, heavy metals*

INTRODUCTION

St. Ana Lake is situated in Romania in the area of volcanic mountain chain Călimani - Gurghiu – Harghita. It represents the unique crater lake in the Eastern Europe formed by water accumulation in the Ciomadu Mare volcano cone. The earliest scientific reports on the volcanic origin of the lake were

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published in 1956 and 1964 [1, 2]. Further the area presents a great geological interest. Some of the newest studies affect the geology of the area to Later Tertiary and Quaternary [3, 4].

Geological drillings revealed two petrologic formations: the deeper layer containing amorphous volcanic glass with andesites and pyroxenes. The second formation is situated at the surface containing amorphous volcanic glass with andesite, hornblende and biotite [5]. However, pyroxene degradation forms several minerals such hornblende and biotite [6, 7] which could be found in the crater soil and gravel. Such soil and gravel forms the sand shore of St. Ana Lake and also covers the formation in the crater depth.

St. Ana Lake was formed exclusively by accumulation of precipitation having no other water sources. The structure of volcano cone is formed by pyroclastic rocks e.g. andesite, and pyroxenes binded with volcanic glass covered with sand and gravel resulted from upper formation's erosion. This structure of the lake's bottom is permeable due to the cracks in pyroclastites causing some water loss. Actually the water level is 6.4 m varying according to the precipitation amount [8, 9]. The average level of 6 m is sustained by an impermeable layer of mud deposed at the lake bottom having the maximum thickness of 4 m [8]. The variation of water level is related only to the infiltration in the shore pyroclastite, gravel and sand.

The rain water presents a high level of purity very close to distilled water with a slighter acid pH due to CO_2 dissolving from atmosphere and this unless there are some pollution traces [10, 11]. St. Ana lake has no other water sources than precipitations so the water in the lake must have physical – chemical properties similar to the distilled water. By natural way there are involved some interactions with shore sand, gravel and respectively with the mud from the bottom of the lake that could affect the water's properties. On the other hand some research mentions some alteration of the local environment due to the intense touristy traffic mainly increased rates of lead pollution [8].

The aim of present article is to investigate the mineralogical composition of St. Ana Lake shore and bottom related to the measured water properties at different depths.

RESULTS AND DISCUSSION

Assuming all considerations concerning closed water systems results that the single minerals involved at St. Ana Lake are the sand shore and the mud from the bottom. The mineral composition was identified by X-ray diffraction analysis. The obtained diffractograms are presented in Figure 1. Both spectra presents well developed diffraction peaks corresponding to the crystalline minerals and a curved baseline due to the amorphous volcanic glass. There were found the following minerals (in order of their amount): potassic feldspar, biotite, hornblende, potassic muscovite, and hydrate silicate for both investigated samples.

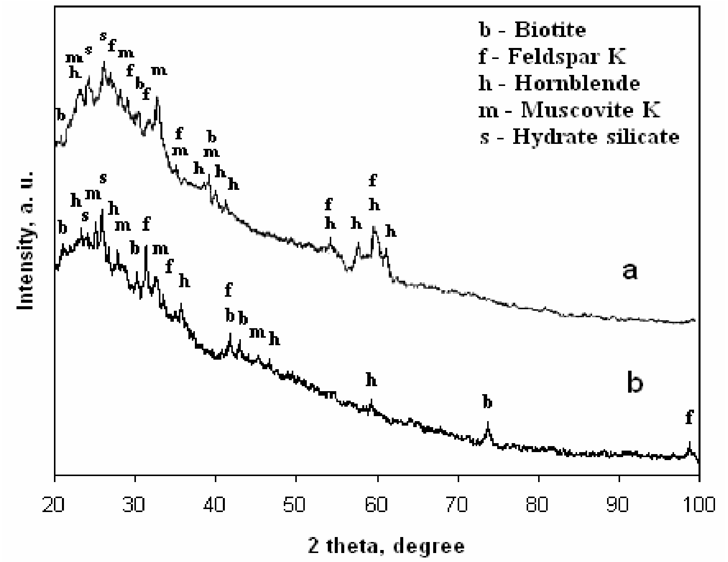


Figure 1. The X ray diffraction spectra for samples collected from St. Ana Lake: a) sand collected from the shore, and b) dry mud from the bottom of lake.

Potassic feldspar is a tectosilicate based on tetrahedral $[SiO_4]^{4-}$ structure with a ¼ amount of Al^{3+} ions which forms extra bounds $[AlO_4]^{5-}$ which fix alkaline ions such K^+ or Na^+. The chemical formula for identified potassic feldspar is: $K(AlSi_3O_8)$. It has a triclinic crystal structure and appears in a bright white color in cross polarized light [6, 12]. This structure is more stabile than inosilicates and phylosilicates. There were found some altered form of potassic feldspar as hydrate silicate which have the chemical formula $K_4(H_4Si_4O_{12})$ [13].

Another important mineral found is the hornblende. It is an inosilicate having simple or double infinite chains of tetrahedral $[SiO_4]^{4-}$ mixed with extra bounds $[AlO_4]^{5-}$. The free valence of Al^{3+} in the chains structure bonds several ions such Mg^{2+}, Ca^{2+}, Fe^{2+}, Fe^{3+}, and others [6]. The chemical formula for identified hornblende is: $Ca_2(Fe_2,Mg)_4Al(Si_7Al)O_{22}(OH,F)_2$. The double chains are very resistant due to SiO_2 units in the tetrahedral silica meanwhile Mg^{2+}, Ca^{2+}, Fe^{2+}, Fe^{3+} ions have weaker bonds [14]. The hornblende sheets appear in a greenish color in cross polarized light.

It was also found a new class of silicate - phylosilicates. They are the result of decomposed tectosilicates and inosilicates. In this case are formed very resistant pseudo-hexagonal planes of tetrahedral $[SiO_4]^{4-}$ bonded by 3 common oxygen molecules. The free valences resulted are perpendicularly oriented to the planes which bounds ions such Al^{3+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, K^+ which assure a monoclinic crystal structure [6]. One of the most important phylosilicate found is the biotite. The chemical formula of biotite is $KFeMg_2(AlSi_3O_{10})(OH)_2$ [15]. We notice the presence of Mg^{2+} and Fe^{2+} ions which gave a shiny black color of biotite crystals, which is also known as black mica. In cross polarized light it features an orange – red color with pleochroism. Similar to biotite we found muscovite, the common mica. The chemical formula is $H_2KAl_3Si_3O_{12}$ [16]. The crystal structure is similar to biotite and the microscopic aspect is bright featuring a yellow colour in cross polarized light.

Figure 2a presents the optical transmitted light microphotograph for the sand shore sample. We observe a wide range of particle size. The occurrence of crystals in the sand is observed in cross polarized light microphotograph. There are revealed large green hornblende particles having at least 75 µm diameter, reddish biotite and yellow muscovite particles with a planar average dimension of almost 100 µm, and several potassic feldspar particle featured in a bright white color having around of 50 µm diameter. There are also observed some traces of fine particles of similar occurrence having at least 10 µm.

In Figure 2b are presented the optical microphotographs for the mud collected from the bottom of the lake. There are revealed formations of very fine particles having the average diameter between 5 and 10 µm. The particle refinement influence the color of cross polarized light where the formations appear in a diffuse light due to the small particle mixture. However there are observed some of bigger reddish biotite and potassic feldspar particles having around of 20 µm diameter [28].

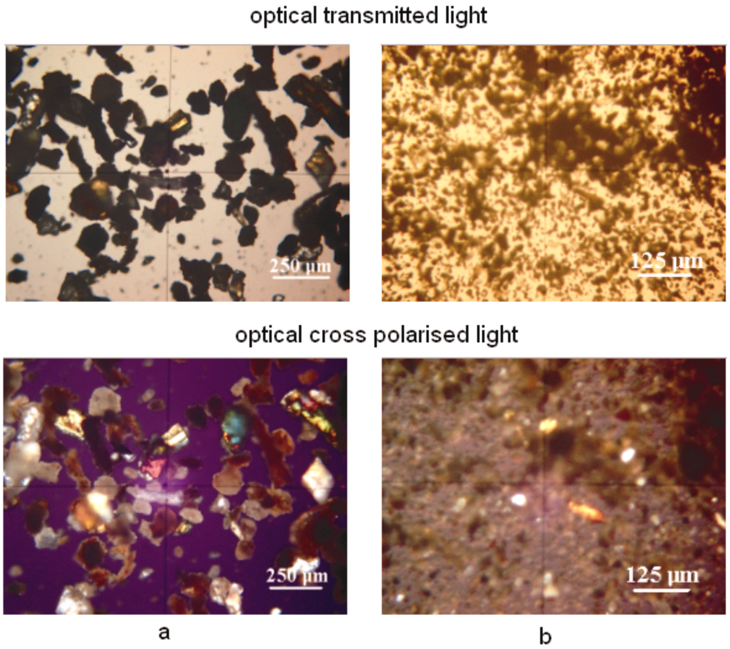


Figure 2. Optical microphotographs for samples collected from St. Ana Lake: a) sand collected from the shore, and b) dry mud from the bottom of lake.

Optical microscopy reveals that the particles of sand are rough micro-scaled particles instead of small particles which are rather found in the mud from the bottom and they have similar mineralogical structure. Small particles of clays and inosilicates are able to release ions at longer exposure in wet environment [17, 18]. Some recent studies evaluate the clays ability of ions releasing in some pH controlled environment. There were noticed the releases of Al^{3+}, Fe^{2+}, Ti^{2+}, and Zn^{2+} in acid environment [19, 20].

We identify the following minerals that which release ions: the biotite, the muscovite, and the hornblende due to their lamellar structure and weaker bonds between lamellae. The main released ions are Fe^{2+}, K^{+}, and Mg^{2+} because of their positions as bonds between pseudo-hexagonal lamellae. Assuming the ions releasing as an emergent hypothesis the water properties of St. Ana Lake will vary according to the particles distribution at different depths.

The quantitative particle distribution measure is given by the average diameter and average percentage density unit. Optical microscopy investigation prove that the water from the surface to 2 m depth is free of micro-scaled particles, but they were found dispersed in water samples from 2 m to the bottom of the lake (4 m), Figure 3.

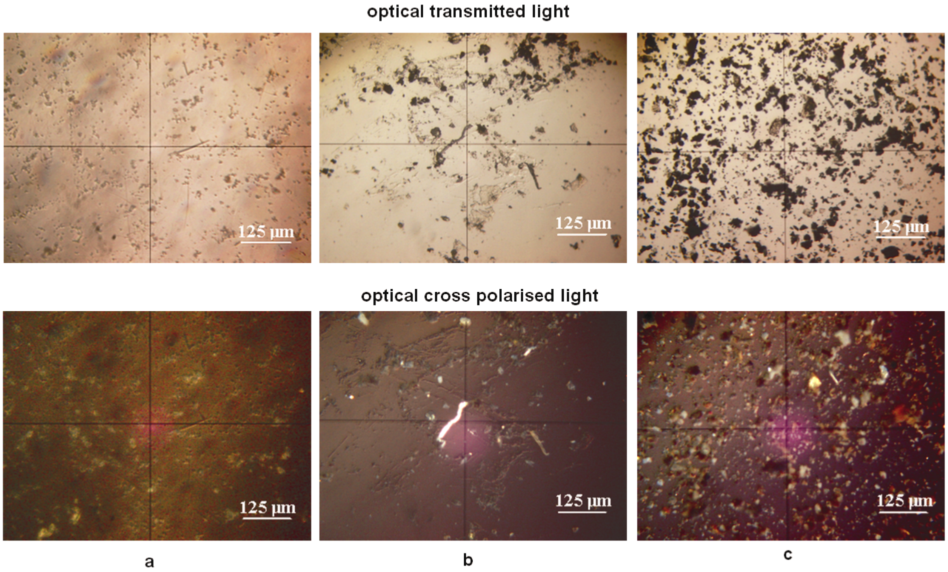
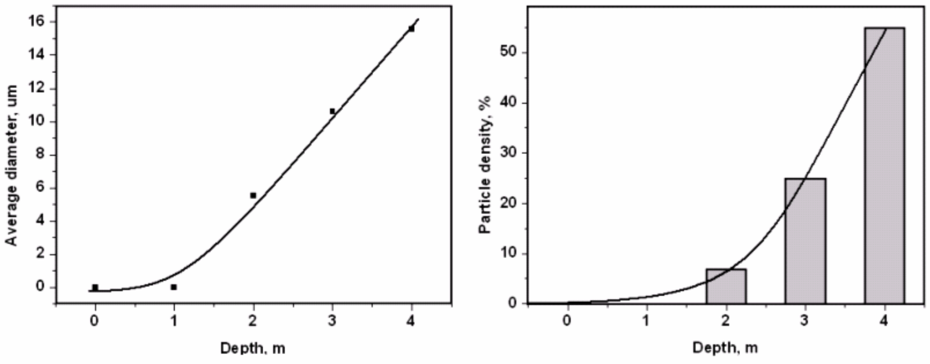


Figure 3. Optical microphotographs for water sample collected from different depths: a) 2 m, b) 3 m and c) 4m.

The optical transmitted light microphotographs of water sample collected from 2, 3, and 4 m depth are presented in Figure 3. At 2 meters we observe, Figure 3a, several very small micro-scaled particles, at 3 m they are bigger and finally at 4 m they are the biggest. In cross polarized light at 2 meters, particles are so small that appears as a low diffused light which could not allow identifying of certain mineral. At 3 and 4 m depth there could be observed in cross polarized light, Figure 3 b and c, some potassic feldspar, biotite and hornblende particles. The quantitative analysis on optical microphotographs was performed by Image J processing soft and the results are plotted in Figure 4.

The particles average diameter variation with water depth, Figure 4a, was correlated with particle density distribution presented in Figure 4b. In the water layer from 0 to 2 m depth were found no micro-scaled particles proving that they are dispersed. At 2 m depth we found an average particle size of 5.53 µm related to a density of 7 %, at 3 m depth the particle average diameter became 10.60 µm related to a density of 25 % meanwhile at 4 m depth the average particle diameter is 14.58 µm corresponding to a density of 55 %. The situation observed at 4 m depth is very close to the mud from the bottom, the observed particle diameter is in good agreement. This difference is due to a lower particle density than in the mud layer.



a b

Figure 4. Particle distribution versus water depth:
a) Average diameter and b) Particle density.

Particle size distribution feature a parabolic shape related to a half – Gaussian distribution of density which means a possibly exponential increasing of water turbidity with water depth. Smallest particles related to a low density, case at 2 m depth, assure a low dispersion of light radiant flux in a turbidity nephelometer, respectively a low amount of scattered light. This situation leads to a low turbidity. Increased particle sizes and their density lead to an average scattered light in a nephelometer, case of 4 m depth, which gave an average turbidity. The usual turbidimeters have two ranges of measurements: for very low turbidity between 0 – 40 NTU (the sensor is set for scattered light) and for high turbidity between 40 – 4000 NTU. For high turbidity measurements it is used the direct light beam attenuation [21, 22].

In Figure 5a is presented the resulted variation of water turbidity versus depth. We observe that all obtained values are below the limit of 40 NTU which means that the water in St. Ana Lake is clear. At the surface and at 1 m depth were obtained turbidity values 2.18 and 2.55 NTU, very low values induced by possible nano - suspensions (e.g. particles with diameter under 100 nm which could not appear at common optical microscopy inspection). The turbidity increases sensibly at 2 m resulting 3.03 NTU, a value still very low. The notable increasing turbidity is between 3 and 4 m depth where it increases from values of 3.55 to 25.7 NTU. This strong increasing is due to the proximity of mud layer. The turbidity variation features a part of a logarithmic shape which probably leads to a constant value in the compact mud layer (a high turbidity domain). Based on the observation in Figure 5a, water turbidity is rather affected by the particle density in the water layers than their size.

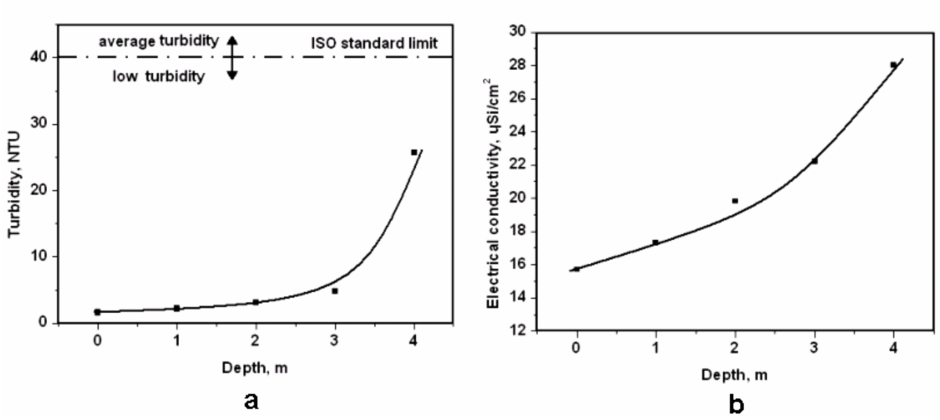


Figure 5. Physical properties of water versus water depth:
a) Turbidity and b) Electrical conductivity.

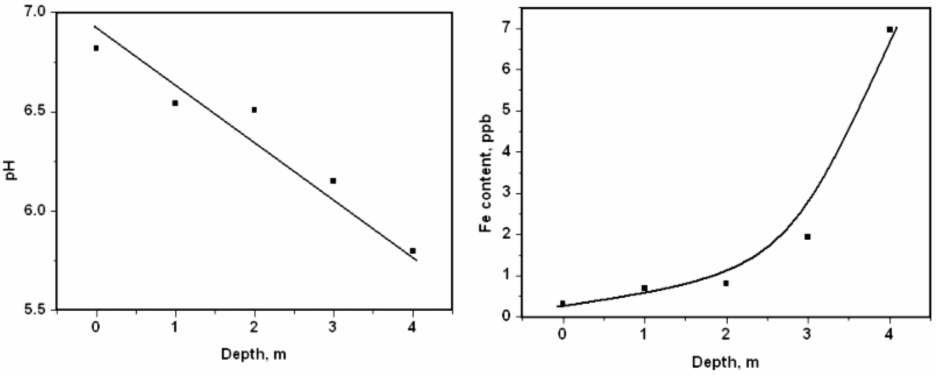
The other main physical property of water is the electrical conductivity. It is affected by salts dissolved in water such carbonates and chlorides. The electrical conductivity increases proportionally to the amount of dissolved solids [23, 24]. Minerals identified for St. Ana Lake shore and bottom mud are not soluble in water so the electrical conductivity must be preserved. However, as mention before minerals such biotite, hornblende and feldspar are able to release ions at longer contact with water, fact favored by a lower pH value [17 – 20].

The only water source of St. Ana Lake is the precipitation (e.g. rainfall and snow) which leads to an electrical conductivity similar to the rain water. This hypothesis is confirmed by the value obtained at the water surface 13.5 µS/cm. The electrical conductivity increases progressively with the suspended particle density resulting 26.8 µS/cm at 4 m depth, value comparable to the well water.

The observed electrical conductivity variation proves the hypothesis of ions releasing, fact confirmed also by the variation of pH and Fe content.

In Figure 6a is presented the variation of pH versus water depth. The measurements points out a pH of 6.82 at water surface close to the neutral value. The pH value is typical for rain water which is slightly lower than neutral because of CO_2 dissolved from atmosphere during the raining [10, 11]. In the precipitation samples, the pH values range from 5.18 to 7.30 [29] and we observed similar values. The pH decreases directly proportional with the water depth resulting at 4 m an acidic value of 5.80. Resulted values are in good agreement with the observations for other inactive volcanic crater lakes [25], while the active ones presents a lower pH due to intensive emission of SO_2 [26, 27].

The observed acidic pH in the lower water layer of St. Ana Lake favors a slow and continuous releasing of Al^{3+}, Fe^{2+}, and Zn^{2+} from biotite, hornblende, and potassic feldspar proving the variation of electrical conductivity without solids dissolvation.



a b

Figure 6. Chemical properties of water versus water depth:
a) pH and b) Fe content.

We want it to prove that St. Ana lake has no pollution. The determined heavy metals were chosen according to the environmental criteria. These heavy metals have a relevant impact on the environment and their absence is a sign that the lake is not polluted.

The most important element involved in identified minerals is the Fe due to its belonging of heavy metals which could be traced. The performed measurements pointed out significant amounts of Fe, but situated far below the maximum admitted level, Figure 6b. At the water surface and 1 m depth the Fe content is under the detection limit which is 2,02 ppm. The Fe content has an increasing tendency with water depth. The strongest increase is observed between 3 and 4 m depth from values of1.94 ppb to 6.96 ppb. Comparing with the turbidity evolution, the water with higher turbidity in St. Ana Lake features also a higher content of Fe.

Heavy metals measurements found traces of Cu and Zn, resulted average values are Cu = 0.03 ppb and Zn = 0.05 ppb. The performed measurements show that in St. Ana Lake at investigation period (July 2010) are no traces of Cd and Pb, the samples results were: Cd is under the detection limit which is 0,17 ppm and Pb is under the detection limit which is 0,084 ppm. This situation is very good for the environment condition and proves a very good improvement from the state reported in 2008 by Duliu et al. [8]

Cu and Zn traced in identified minerals are in very low amounts. Because Cd and Pb are missing, the observed traces of Cu and Zn are rather found by natural reasons (similar to Fe content) than due to some pollution sources.

All measurements prove that the water properties of St. Ana Lake varies with water depth in a naturally manner due to the distribution of mineral particles suspended in water layer. At the investigation time, July 2010 results that there are no traces of pollution in aquatic environment.

CONCLUSIONS

The minerals identified in the sand shore and mud from the bottom of St. Ana Lake is: biotite, potassic feldspar, hornblende, potassic muscovite, and hydrate silicate mixed with amorphous andesite. Such mineral particles were observed suspended in the water from an average depth of 2 m to the bottom. We found that the electrical conductivity is close to the distilled water for the upper layers and increases to the bottom due to the dissolved mineral ions, mainly Fe^{2+}, released by phylosilicates and tectosilicates (e.g. biotite and hornblende). The turbidity is very low at the surface and progressively increased at 4 meter depth, because of the particle density variation in lower water layers. The pH is in an acid range having a slight decreasing with the water depth due to the acid pH of phylosilicates. The main metal found is Fe, the concentration is considerably under the standard limit. It increases with water depth due to the increasing of biotite and hornblende particles floating in water. There were also identified traces of Zn and Cu in very low concentrations and no traces of Pb and Cd. All measurements performed in July 2010 prove that the St. Ana Lake presents a normal state for a closed water system with no pollution trace.

EXPERIMENTAL SECTION

The sand samples were collected from all exposed shore and mixed into an average sample representative for all regions. Mud samples were taken with a manual dredge from several points and mixed into a representative sample which was naturally dried.

Representative average water samples were extracted with a specific device from top of water and from 1, 2, 3 and 4 m depth. Water samples were transported to the lab in proof well sealed plastic bottles. Water samples were preserved with 1% HNO_3 until conductivity and pH measurements were taken.

The sand and mud samples were investigated by X – ray diffraction analysis using a DRON 3 diffractometer improved with registering module and professional analyzing soft. It was used a Co $k_{\alpha.}$ monochrome radiation. Diffraction peaks identification was done using standard database MATCH edited and compiled by Crystal Impact.

Sand, mud and water samples were inspected by optical transmission light and cross polarized light using a Laboval 2 mineralogical microscope produced by Carl Zeiss Jena.

Electrical conductivity and pH were measured with HI 255 Combined Meter & EC/TDS/NaCl Hanna Instruments. Turbidity was measured with a turbidity meter 4193414, Hanna Instruments. Water samples were preserved with 1% HNO_3 until conductivity and pH measurements.

The metal content was measured by emission spectrometry / flame atomic absorption AAS Sens Spectrophotometer, GBC Australia. For the heavy metals determination, water samples were prepared as following: take 50 ml of water and bring to dry, then resume with 10 mL 0.5 M HNO_3. The used wavelengths are: for Cu - 324,70 nm, for Fe - 248,30 nm, for Zn - 213,90 nm, for Pb - 217,00 nm and for Cd - 228,00 nm. Each sample determination is repeated three times by the device. The results are the average readings. The quantitative determination is made based on calibration curves constructed with standards.

REFERENCES

1. D. Slavoaca, C. Avramescu, *Academia R.P.R., Comunicari,* **1956**, *VI.* 3.
2. A. Lazar, E. Arghir, *Comunicari Geologice,* **1964**, *vol L/2*, 87-101.
3. S. Szakacs, I. Seghedi, *Acta Vulcanologica*, **1995**, *7*, 145–153.
4. D. Karatson, *Zeitschrift fur Geomorphologie*, **1999**, *114*, 49–62.
5. I. Seghedi, A. Szakacs, M. Kovacs, E. Rosu, Z. Pecskay, Sed inst. Geol. Geof., **1995**, *76*, no.7, 49-50.
6. G. Arghir, L.M. Ghergari, Cristalografie – Mineralogie Indrumător de lucrări de laborator, Litografia Institutului Politehnic din Cluj – Napoca,**1983**.
7. I. Seghedi, H. Downes, Z. Pecskay, M.F. Thirlwall, A. Szakacs, M. Prychodko, D. Mattey, *Lithos*, **2001**, *57*, 237.
8. O. Duliu, T. Brustur, Ş. Szobotka, G. Oaie, C. Ricman, V. Alexe, M. Iovea, S. Hodorogea, *Geo-Eco-Marina,* **2008**, *14, supliment nr. 1,* 181.

9. A.G. Pilbath, Z. Pal, Microregiunea Ciomad-Balvanyos, Ed. Green Steps România, **2007**.
10. I. Haiduc, Chimia mediului ambiant. Controlul calității apei, Ed. Universității Babeş-Bolyai, Cluj-Napoca, **1996**, 61.
11. G. B. Lawrence, *Atmospheric Environment*, **2002**, *36*, 1589.
12. ***, Feldspat potassic, Match Diffraction Database, Match PDF # 89-8572, Crystal Impact, **2008**.
13. ***, Potassic Hydrate Silicate, Match Diffraction Database, Match PDF # 72-1101, Crystal Impact, **2008**.
14. ***, Hornblende, Match Diffraction Database, Match PDF # 71-1060, Crystal Impact, **2008**.
15. ***, Biotite, Match Diffraction Database, Match PDF # 80-1106. Crystal Impact, **2008**.
16. ***, Muscovite, Diffraction Database, Match PDF # 02-1019. Crystal Impact, **2008**.
17. F. Tateo, V. Summa, M.L. Giannossi, G. Ferraro, *Applied Clay Science*, **2006**, *33*, 181.
18. F. Tateo, V. Summa, *Applied Clay Science,* **2007**, *36*, 64.
19. J.R.O. Kikouama, K.L. Konan, A. Katty, J.P. Bonnet, L. Baldea, N. Yagoubi, *Applied Clay Science*, **2009**, *43*, 135.
20. F. Tateo, A. Ravaglioli, C. Andreoli, F. Bonina, V. Coiro, S Degetto, A. Giaretta, A. Menconi Orsini, C. Puglia, V. Summa, *Applied Clay Science*, **2009**, *44*, 83.
21. ***, EPA, Quality criteria for water, *Office of Water Regulations and Standards*, Washington DC 20460, U.S., **1986**.
22. ***, Water Quality – Determination of turbidity, *ISO European Standards*, EVS-EN ISO 7027:2000, **2000**.
23. D. Masterman, K. Redding, Water Quality with Vernier*, Vernier Software & Technology Guidelines*, **2006**.
24. I. Chicinaş, N. Jumate, V. Pop, Fizica materialelor metode experimentale, Presa Universitară Clujeană, Cluj-Napoca, **2001**.
25. J.C. Varekamp, G.B. Pasternack, G.L. Rowe Jr, *Journal of Volcanology and Geothermal Research*, **2000**, *97*, 161.
26. B.W. Christenson, *Journal of Volcanology and Geothermal Research*, **2000**, *97*, 1.
27. M. Martınez, E. Fernandez, J. Valde, V. Barboza, R. Van der Laat, E. Duarte, E. Malavassi, L. Sandoval, J. Barquero, T. Marino, *Journal of Volcanology and Geothermal Research*, **2000**, *97*, 127.
28. Ramona-Flavia Câmpean, Dumitru Ristoiu, George Arghir, Aspects Concerning the Nano-Sediments Compozition and Distribution in St Ana Lake-Romania, *Studia UBB Ambientum*, **2009**, LIV, 1-2, p. 11.
29. ***, Raport privind starea factorilor de mediu în județul Harghita, Semestru II, 2010, Ministerul Mediului şi Pădurilor, Agenția Națională pentru Protecția Mediului Bucureşti, Agenția pentru Protecția Mediului Harghita Miercurea Ciuc.