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FACULTY OF ENVIRONMENTAL SCIENCE AND ENGINEERING

Ph.D Thesis Summary

STUDY OF PHYSICO-CHEMICAL PROPERTIES OF SEDIMENTS AND SUSPENSIONS OF SEVERAL LAKES FROM TRANSYLVANIA

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CONTENT

Keywords*: sediments and suspension, Transylvanian Basin, Saint Ana Lake, Badenian salt, Pata Rât Lake*

Chapter. I. Introduction

Shortly after the Earth formation, soil and water were the reference elements that have made possible the appearance of life, by the particular relationship they inter-relate. If the crust ,,Lithos", offers the solid material that supports things being alive, the water intervenes decisively, directly contributing to the diversification of life forms. The main objective of this study is the lakes, the particular relationship between water and surface crust, located within the continents.

The Transylvanian Basin has a specific geology grace to Paratehtys Sea evolution since the middle Miocene, involving mainly the Burdigalian Badenian -Sarmatian period, different specific lithologies such as carbonate or evaporitics (Filipescu, 1997, 2005; Huismans, 1997; Davor, 1998; Zorn, 2004). This geological diversity controls the presence of various types of lakes in the Transylvanian Basin.

In terms of altitude, they are found plains lakes or hilly natural lakes and also many anthropogenic lakes such as ponds and filling lakes specific to hydrological regularization. It is also noted the presence of salt lakes due to the presence of the Badenian salt accumulation in the substrate. Thus we can mention the dissolution lakes of diapirs, such as salt lakes from Sovata (Alexe, 2006). It can be mentioned in the same category the salt lakes from Turda, Cojocna (Cluj county), or some Mureș Valley lakes (Arthur, 2006). These lakes are often *open water systems*, having at least one headwater source and are drained by rivers or *semi-closed systems* and they have as water source a source, but due to a modest influx of water which can not provide a flow as rivers or streams, they do not have apparently any drainage of the type specified above. A special category of lakes is represented by *closed systems* which are without a *headwater source* such as a spring or a drainage system as rivers flowing, but are fueled exclusively by precipitation. We can rightly call them *endorheic lakes*. The closed water systems may present special features in terms of soil-water relationship, and furthermore in sedimentable and suspended particles. A type of location that favors the formation of such closed systems is the inactive volcano craters. In our country there is such an unique lake in Europe, named St. Ana Lake. Research on developing this thesis has the aim to investigate this lake in terms of ground-water interaction, and also the particles in suspension.

Chapter. II. Sediments and suspensions în lakes

The subject of this thesis is to observe and study the physicochemical properties of sediments and suspensions in some lakes in Transylvania. From the above so far is mostly about two important aspects: sedimentation as process in formation of sedimentary rocks and as physical actual process taking place in lakes.

The biogenic sediments are the consequence of the existence of water bios like fish, molluscs, plants and microorganisms. Given these aspects on biogenic nature sediments should be considered the interaction of the bacterial environment on the sludge formed on the bottom of lakes. This naturally aspect can be a potential risk factor in combination with pollutant discharges which may affect the aquatic food chain and moreover the human health. It can be also observed organo-chemical and organo-metallics compounds as recent studies have shown (Ristoiu et al., 1998; Ristoiu et al., 2009, Kovacs et Ristoiu 2009a, 2009b)

Chapter. III. Specific methods of investigation

When we talk about some natural or synthetic material we can approch the composition and / or the structure. The composition shows us whereof that material is made and the structure shows us how the material is organized. Thus we can speak of the chemical composition of the target material that will indicate exactly what atoms occur and in what quantity. Then we can talk about the phasic composition where we discuss the groups of atoms formed in crystalline phases or molecules where we can also talk about composition, which have implicitly defined a specific structure.

Given this hierarchy of the composition according to the structure, there are specific methods of investigation for each of these units of specified structure in the material. Usually the chemical analysis provides information on chemical composition, often showing quantitative by analytical methods the elemental content of the sample, but obviously and the molecules of the investigated material. Other methods such as X-ray diffraction, can identify the phase composition of a material without appel to its chemical properties but the specific physical properties.

Chapter.IV. Transylvanian Basin Geology

Through genesis and geological structure, followed by gliptogenesis, Transylvanian Basin is outlined as geological and structural unit of the Romanian Carpathians Orogen. Orographic speaking, corresponds to a plateau, bordered by depressions and submountaine hills, represented measurably as sub-Carpathian structures.

Sedimentary basin deposits are disposed over distored structures resulted during alpine cycle (eg Dacide and Transilvanide fragments). The first sedimentary megasequence is at maastricthian terminal-eggenburgian interval. It includes alternates of epicontinental marine formations with continental formations (Rusu, 1970; Proust et Hosu, 1994; Hosu, 1999; Gheerbrant et al., 1999; Codrea et Hosu, 2001; Codrea et Dica, 2005). In some cases, the continental formations may obtain lateral continuity with transitions to marine basin areas (Filipescu et Kaminski, 2008).

In the series of sedimentary deposits which are forming the Transylvanian Basin have been distinguished three cycles of sedimentation: Upper Cretaceous, Paleogene and Neogene (Ciupagea, 1970).

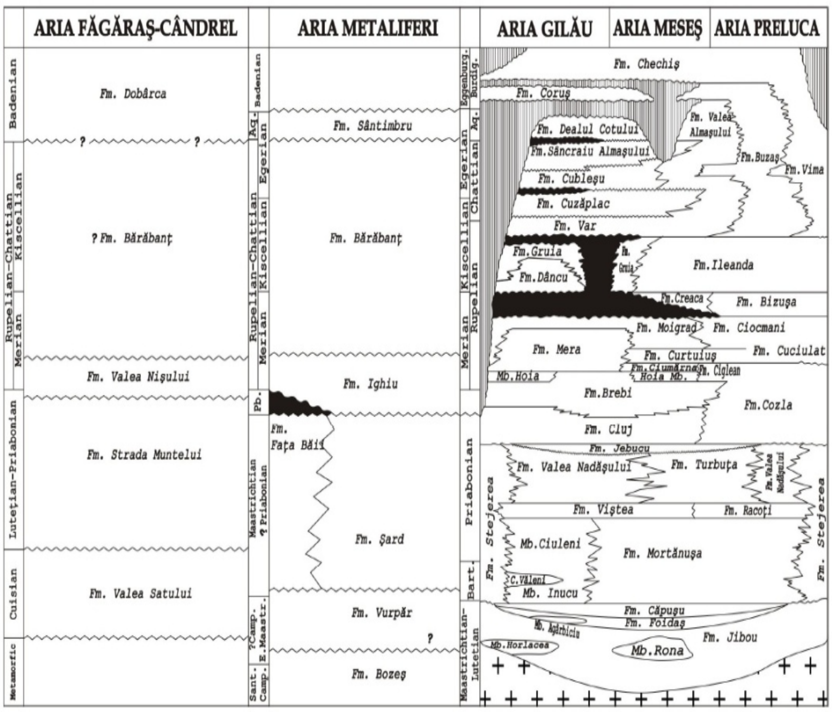


Fig. 1. The correlation of the geological formations of the Metalliferous area and NW Transylvanian Basin during the Cretaceous-Early Miocene (last, according Rusu 1987, 1989, updated by Filipescu, 2001)

Natural and anthropogenic premises in genesis and distribution of salt lakes in Transylvanian Basin

To understand the formation of spatial mechanism of the lake units of the Transylvanian Basin we consider necessary a careful analysis of some of the most important natural factors that formed the basement of their genesis: geological and geomorphological factors, especially the formation and the occurrence near the surface of salt deposits. The paleogeographical evolution of the basin is divided into three main stages: pre-basinal or pre-badenian, basinal (Badenian-Pannonian) and gliptogenetic (post-Pannonian) (Alexe, 2006).

The geological structure of the volcanic sector Călimani-Gurghiu-Harghita

The Transylvanian Basin and the Eastern Carpathians means equally structures resulted from the specific Alpine Orogen Carpatho-Pannonian system, which is positioned close to the western edge of the Eurasian plate, involving at least two smaller lithospheric blocks such as Tisia-Dacia and ALCAPA blocks (Balla , 1987; Csontos et al., 1992; Csontos, 1995).

The volcanic chain Călimani -Gurghiu-Harghita (abbreviated CGH), which occurs along the eastern edge of the Transylvanian Basin is the south-eastern segment of the Carpathian volcanic arc (Seghedi et al., 2004b). It consists of adjacent alignments closely spaced volcanic edifice by the NW-SE.

Chapter.V. Sediments and suspension investigations of Saint Ana Lake

At the eastern edge of the Transylvanian Basin on the boundary limit of Harghita and Covansna lies the Great Ciomadu massive, mountain of volcanic origin. In its crater is one of the most representative lakes with volcanic substrate from Europe, the St. Ana Lake. It is located at 46.12 degrees north latitude and 2`5.88 degrees longitude as can be seen in figure 2.

The lake was formed in the crater of Great Ciomadu massive from the volcanic chain Gurghiu - Harghita placed at his south-eastern limit on the border of Harghita and Covasna county (Gâştescu, 1971).

The Ciomadu Massive, with 1301 m height, is situated in South Harghita Mountains of Eastern Carpathians, which is the southern termination of the volcanic chain Călimani-Gurghiu-Harghita. The Ciomadu is a unitary volcano, but with two craters: well preserved St. Ana and the old, more eroded and cracked, Mohos. The St. Ana Lake age has not yet been precisely determined. Some different researchers place the last eruption at 32 ka (Juvigne et al. 1994) and 10.5 ka BP (Morya et al. 1996) or 9.8 ka (Magyari et al. 2006). The St.Ana Lake is in the bottom of a quasi-circular depression with strong inclined slopes at a depth of 100 m to the lowest saddle and to the surrounding peaks over 200 m.

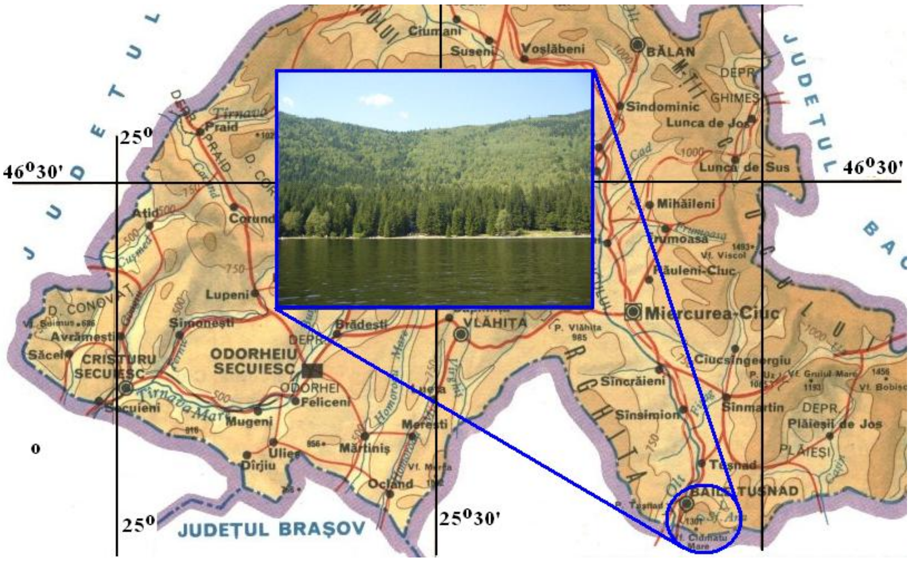


Fig. 2. Geographic location of Saint Ana Lake (Harghita county map).

The significant amounts of precipitation are the reason for the accumulation of water in great amounts in the crater funnel of Great Ciomadu Mountain. From the analysis of the water balance is ascertained that in conditions of a water excess, the lake should record a gradually level increase because it has no surface drainage, which can be observed on the hypsometric map and satellite view, figure 3.

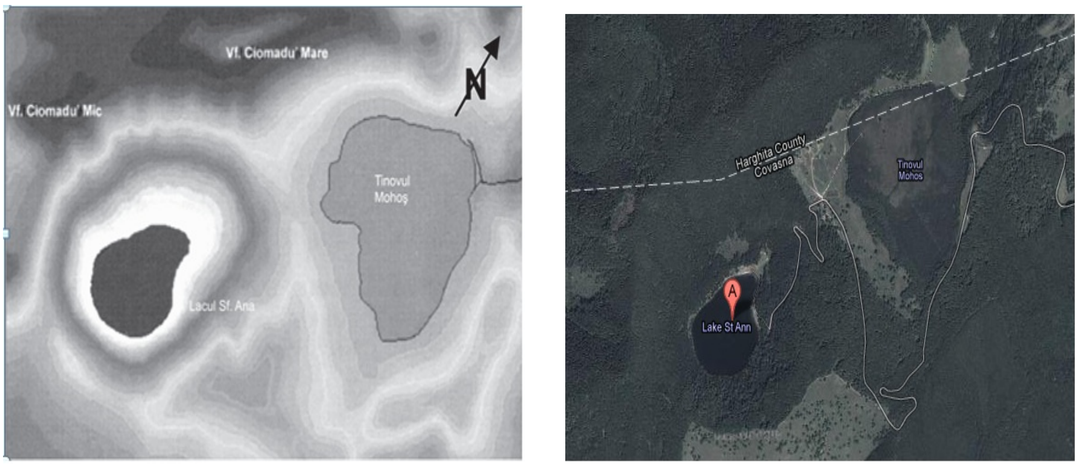


Fig. 3. The hypsometric map (left) and satellite view(right) of the two craters of Great Ciumadu massive (after Pilbath & Pal, 2007)

5.1. Soil investigations

These specific investigations refer mainly to the soils mineralogical composition and the constituent particles morphology. In terms of pedology, the specific pyroclastics of Great Ciomadu volcano present a great amount of mineral particles of different grains slight bonded with organic components such as humus.

Soil sampling

The most representative soil samples of St. Ana Lake are located in the proximal area of the shore which forms a specific beach as shown in figure 4. The specific shore deposits are those who interact directly with the lake water, being mostly able to form suspensions and sediments in the water lake.

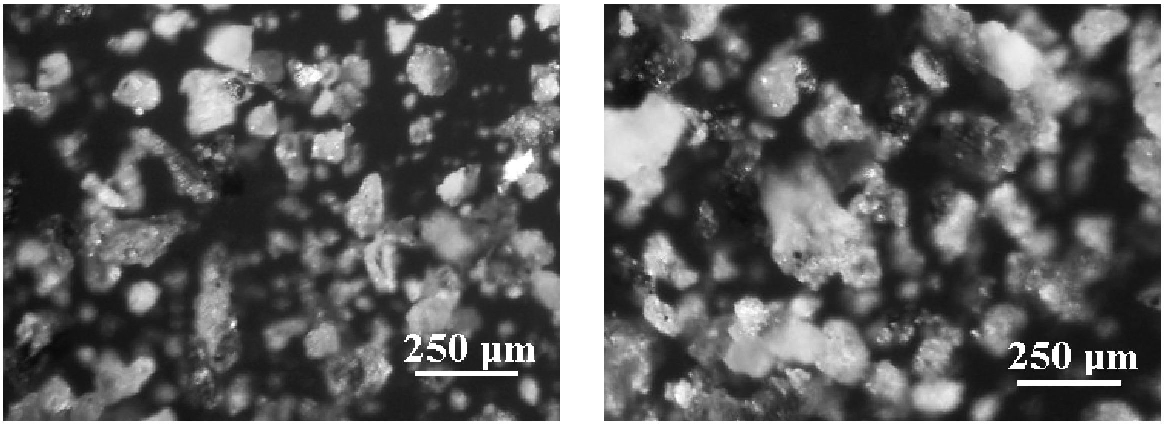
Fig. 4. The shore of Saint Ana Lake: a) overview, b) detail.

As we can see in figure 4 b the most representative soil samples are: beach sand, with average particles less than 1 mm diameter; pebbles located in the proximal vegetation with average particle of several mm diameter and boulders with various sizes of a few cm to over 1 m. Therefore were removed representative samples of sand, fine gravel and coarse gravel according to Attenberg classification.

Another representative sample of soil is the mud from the lake bottom. This was taken from five different points located within the average depth (4 meters) using the liquid sampler. It was brought in powdery state by evaporating the water, not by boiling in order to avoid the damages of sensitive components thereof.

Crystallographic and mineralogical characterization

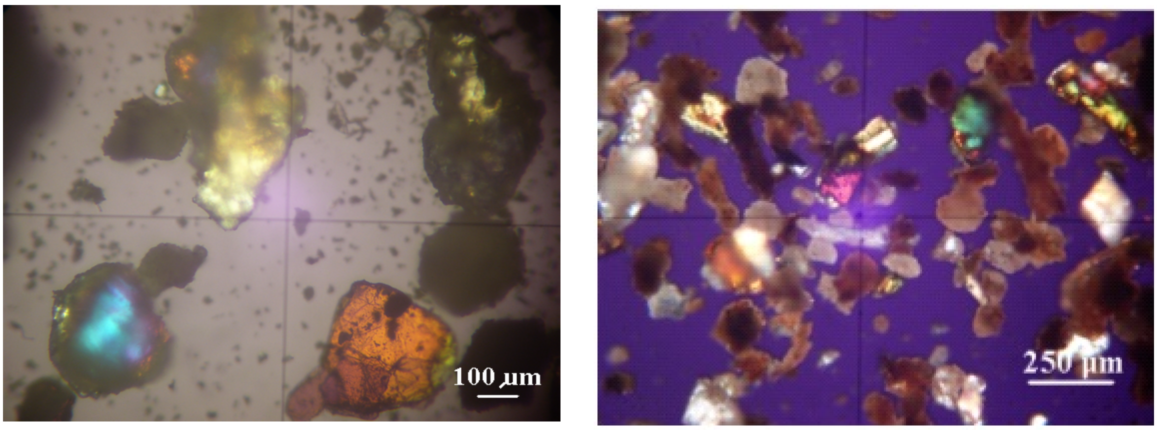
The representative sample of sand: In figure 5a and b are presented the dark field microphotographs of average sand sample (sampling year 2008). We can observe particles of different grains with morphological varieties. On particles larger than 250 µm, we can observe some dark points and some lighter ones, which mean that the particles can have mineralogical associations. These points can be crystals included in amorphous mass.



a b

Fig. 5. Morphological aspects of the average representative sand samples, dark-field optical microscopy, samples: a) in 2008 and b) in 2009.

We can observe in polarized light with the analyzer and the polarizer places an intense red staining of biotite particles showing a darkening at the rotation (extinction) to a specific angle of mica, figure 6. Therefore in the sand of St. Ana Lake shore there are both microscopic and macroscopic particles of biotite embedded in amorphous mass.



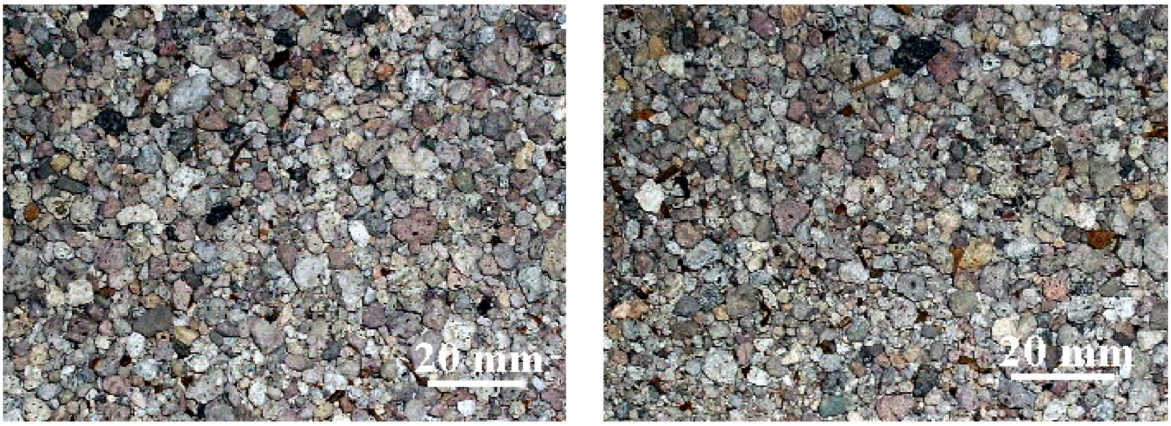
a b

Fig. 6. Sand particles of Saint Ana Lake shore in polarized light: a) 2008 and b) 2009.

Thus, the sand of St. Ana Lake shore contains biotite, muscovite, potassium feldspar and potassium hornblende. Therefore, a characteristic of vulcanites of Ciomadu massive are the potassic silicates. (Câmpean et al. 2009c, Câmpean et al. 2011)

The representative sample of fine gravel

The fine gravel samples were collected in 2008 and 2009. Each is the result of the sampling from five different points on the shore of St. Ana Lake, was similarly prepared like sand samples. Their macroscopic aspect can be seen in figure 7.



a b

Fig. 7. Representative fine gravel samples of the St. Ana Lake: a) 2008 and b) in 2009.

From figure 7 results a macroscopic range distribution of fine gravel particles ranging from 2-3 mm average diameter up to about 10 mm. The X-ray diffraction analyzes were carried out under optimal setting determined by previous research, using this time an anticathode of Cu, respectively the monochromatic radiation Cu kα. The resulted diffractograms for the representative samples of fine gravel are presented in figure 8. (Câmpean et al. 2012).

The diffractogram of the representative sample of fine gravel, taken in 2009 is shown in figure 8.b. Have been identified the same minerals component with the same considerations of diffraction peaks, being observed only some minor changes in their relative intensities, favoring their development for certain crystallographic planes at the detrimental of others.

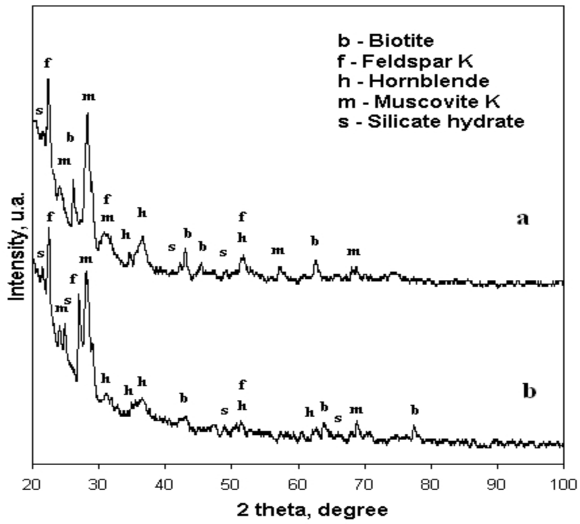


Fig. 8. The resulted diffractograms for the fine gravel representative samples: a) sampling 2008 and b) sampling 2009, using Cu kα radiation.

These small differences are insignificant and can conclude that fine gravel samples taken in 2008 and in 2009 are completely identical, both in morphology and in terms of mineralogical composition (Braşovan et al 2011, Câmpean 2009 b).

Representative sample of coarse gravel (boulder)

As previously, at the St. Ana Lake shore is gravel in a very wide dimensional range from boulders with diameters of 50-100 mm, to boulders up to one meter. Therefore were identified two main types of rocks: with red shade and with green shade. (Câmpean et al. 2012).

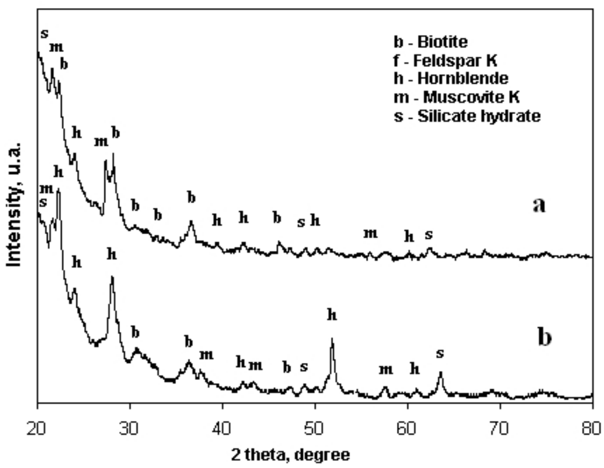
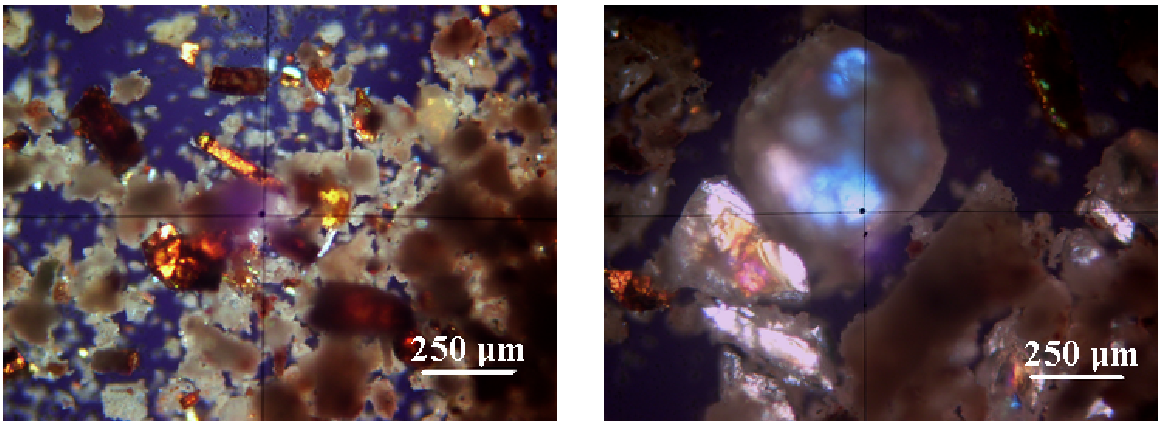


Fig. 9. The diffractograms resulted for gravel on the Saint Ana shore: a) rock with red shade, b) rock with green shade, using Cu kα radiation.

In the diffractogram resulting for the red rock, figure 9.a is obvious the maximum biotite peaks prevalence accompanied by muscovite and with traces of hornblende and silicate hydrate.

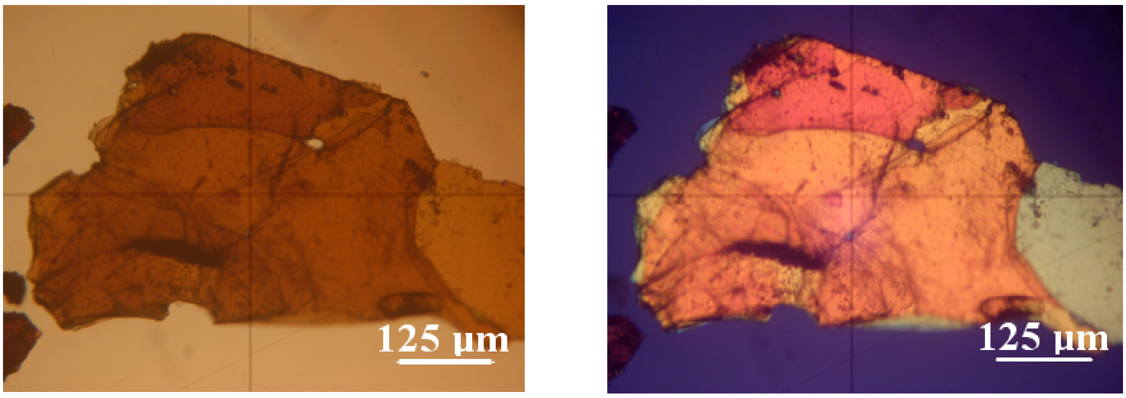


a b

Fig. 10. Optical microphotographs in polarized light with crossed nicols for curd rocks: a) red b) green

In figure 10.a, it can be observed in polarized light with crossed nicols biotitics slides from curd samples of red rock. They have a tabular-lamellar aspect with pleochroism, the color ranging from deep orange to reddish brown depending on their position to the optical axis of the microscope.

For the green rock, prevails the hornblende maximum in X-ray diffraction spectrum from figure 10.b. This indicates a high content of hornblende in green rocks.



a b

Fig. 11. Mineralogical optic microphotographs for a slide of biotite observed in: a) transmitted light and b) polarized light with crossed nicols.

So, we extracted from a red rock a macroscopic crystal sample of biotite which has subjected to disintegration by applying mechanical tensions on the tabular-lamellar aggregate.

The biotite sheets cleaved and broke in very fine slides which were investigate at the mineralogical optical microscope resulting the images from the figure 11. It is observed the typical pseudohexagonal habitat of the biotite and its pleochroism (Arghir, 1986; Rickwood, 1981; Câmpean et al., 2011). The X-ray diffraction analysis performed on the biotite slides extracted from the rock red, indicates the specific maximum peaks as shown in figure 12.

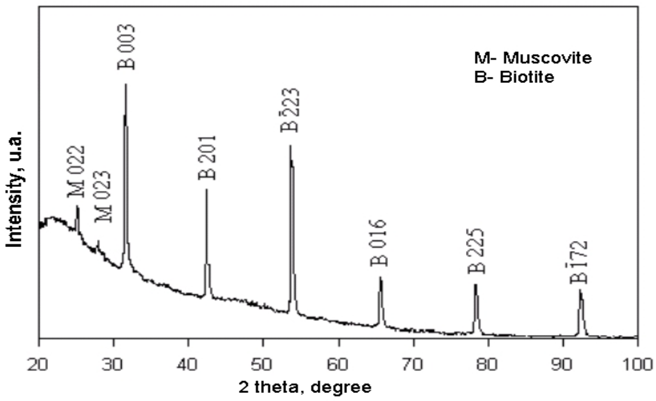


Fig. 12. The diffractogram obtained for extracted biotite sample, using Co kα radiation.

Representative average sample of sludge

The sludge samples were collected in 2009 from five different points in St. Ana Lake at 4 meters depth. These were wet collected and were left to dry in natural conditions to avoid the possible distortions of the sample by heating. As expected the mineralogical composition of the sludge on the bottom of the lake is completely identical to that of the sand from the shore, figure 13.

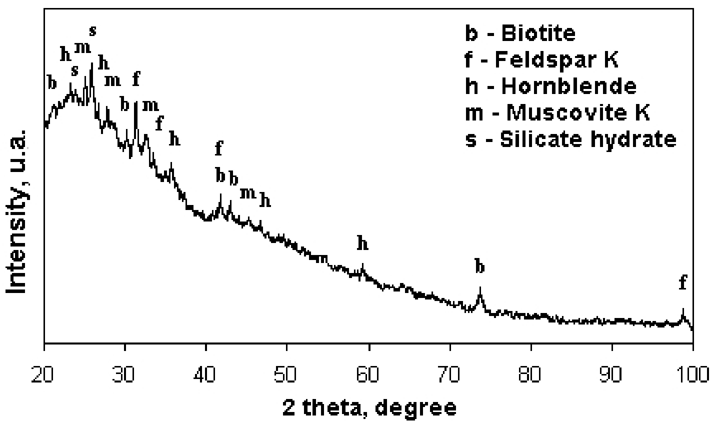


Fig. 13. The diffractogram of the sludge sample taken from Saint Ana Lake from 4 m depth, using Co kα radiation.

Morphological soil particles patterns

The morphological aspects of identified minerals in sand, respectively the mud of the St. Ana Lake may present some features that can facilitate their dispersion in aqueous environment. Of these, the most interesting are the minerals belonging to class of phylosilicates such as the muscovite and the biotite due to their fragmentation ability into ultrafine particles under low mechanical request (Câmpean, 2011; Câmpean, 2012). These ultrafine particles can be easily trained into aqueous environment, which can be maintained in suspension for a long time.

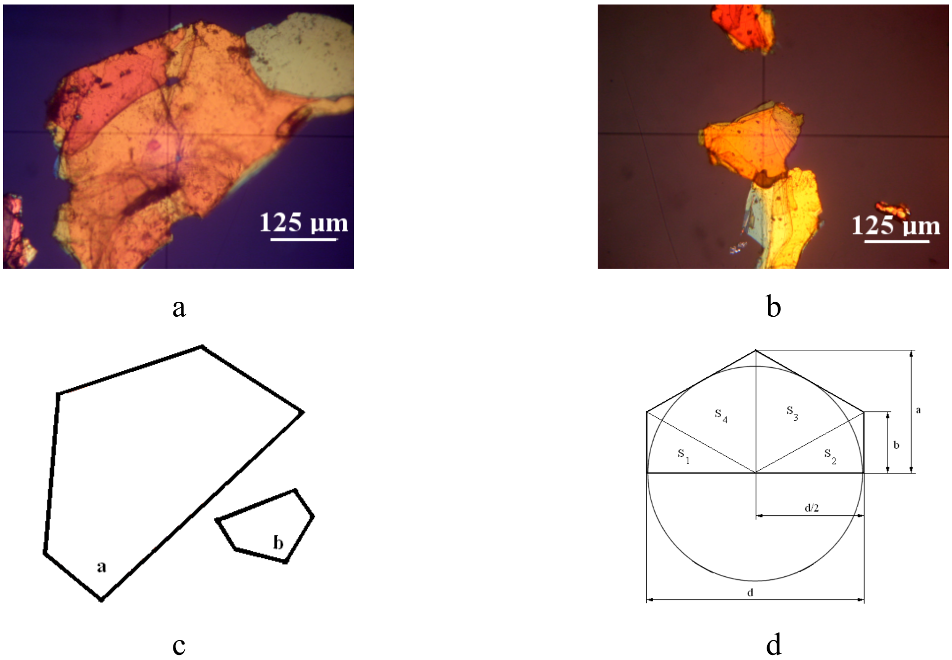


Fig. 14. The geometrical model from biotite slide: a) a larger particle, b) two smaller particles, c) revealed geometric shape and d) geometric model of the biotite particle.

Given the law of Archimedes, the general knowledge of sedimentary particles, takes into account a spherical approximation to a microscopic scale. Therefore in what follows we develop a tabular pattern, starting from highlighting the biotite particles. In figure 14 we started the biotite shape analysis of particles from their overall shape (figure 14 a and b) embodying their exact contours. Based on the revelation of the contour in figure 14.c, was developed a geometric model shown in figure 14.d.

Consider the specific geometric shape of biotite slades as half a hexagon. This geometric shape presents the planar relations of the biotite slade as the tabular model, figure 14. This geometric shape presents the planar relations of the biotite slade as the base of the tabular model, figure 14.

Thus, if the ascending force is smaller than the particle weight, it will sink, and if the ascending force is greater than the particle weight, it will float. In stationary aqueous regime, as occurs in St. Ana Lake, the sedimentation of the observed mineral particles is a matter of time.

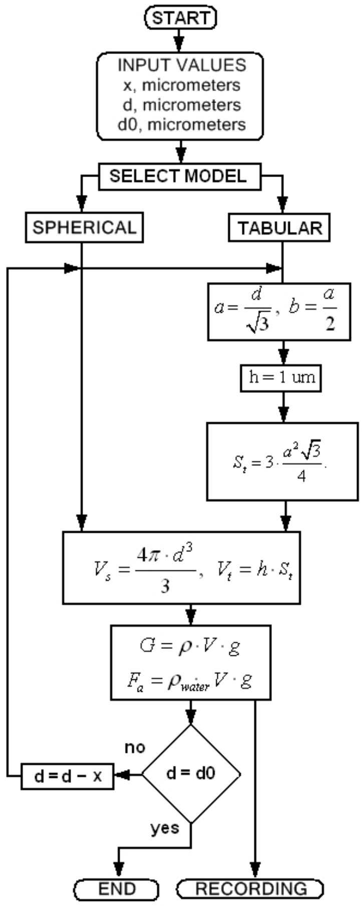


Fig. 15. The flowchart design for the sedimentation algorithm of particles specific to tabular model.

Therefore it is interesting to observe the ascending force variation and the particle weight under different conditions. For this, we developed an algorithm based on the tabular model and also one on the spherically. The flowchart design of this algorithm is shown in figure 15.

5.2. Soil-water interrelationship investigations in Saint Ana Lake

Sampling and sample preparation: The water samples were collected using a device with glass container and manual pumping mechanism. Thus were collected the representative water samples from surface and 1, 2, 3 and 4 m depth from at least five different points located in the area of St. Ana Lake. In the sampling period in August 2009, there was no reported precipitation before 2 weeks, so the lake water was not influenced by currents that could have interfered with particles from the lake bottom.

Highlight the microstructure

The optical microphotographs in transmitted light and in polarized light for water samples taken from 2, 3, and 4 m are presented in figure 16. At two meters is observed some very fine microscopic particles, figure 16, at three meters this are higher and at four meters it can be seen the largest particles in aqueous suspension, figure 16 b and c (Câmpean et al. 2011)

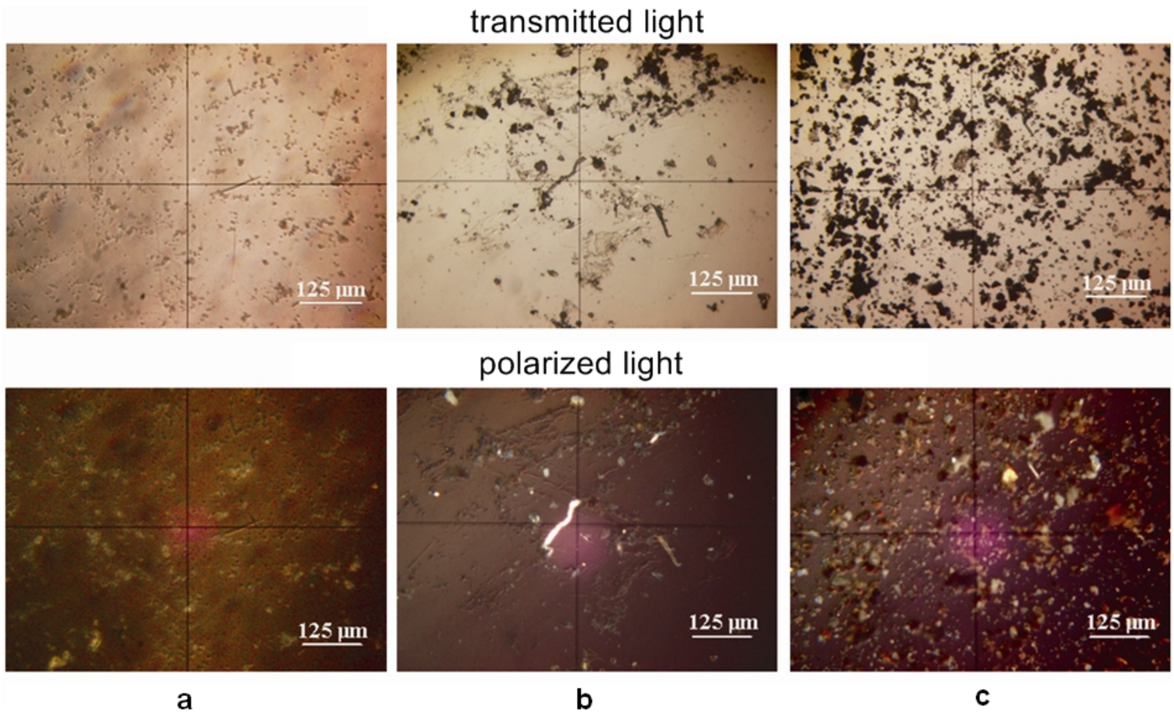


Fig. 16. Optical microphotographs for water samples from different depths: a) 2 m, b) 3 m and c) 4 m

Highlight the nannostructure

Atomic force microscopy (AFM) is the most modern and efficient method for visualization and investigation of nanostructures pretending as a wide range of samples from thin films to nano and microcrystalline powders (Baselt, 1993; Wiesendanger, 1994; Duborg, 2000; Stark, 2001). The AFM images were obtained in tapping mode using an atomic force microscope - Nano Scope type. It was used a type of cantilever with silicium nitride, NSC 12 type produced by Micromasch. The images were recorded on an area of 2.5 x 2.5 μm^2 being done some detailing as shown in figure 17. (Câmpean et al. 2009b).

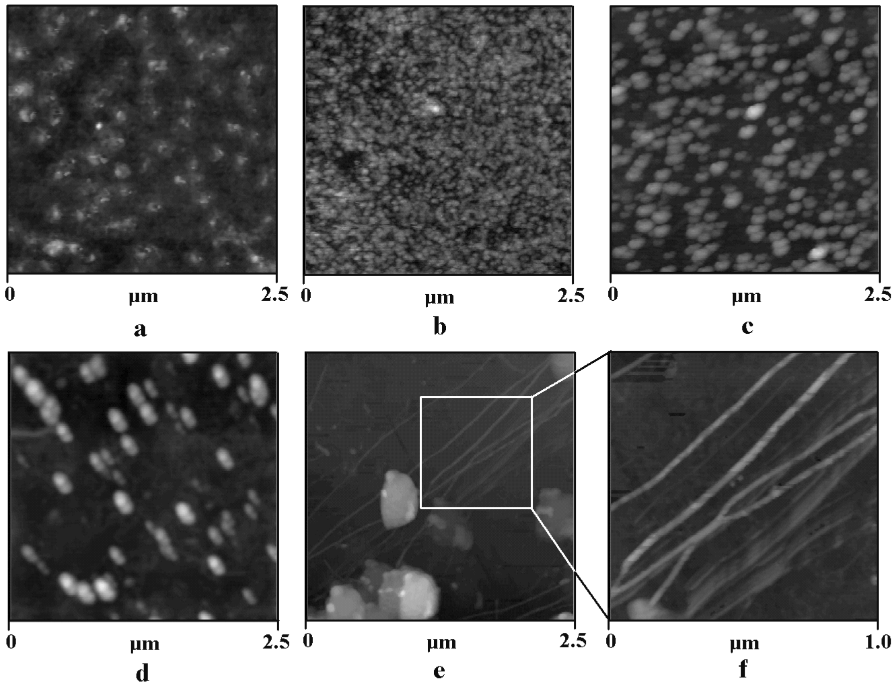


Fig. 17. AFM topographic images: a) glass substrate, b) surface water, c) water to 1 m, d) water to 2 m, e) water at 3 m and f) image detail for water sample from 3 m deep.

5.3. Hydrological investigations

The conductivity and the electrical resistivity: The conductivity for aqueous solutions is influenced by the concentration of substances, the dissolved salts in water favors its increasing conductivity. The Fe^{2+} ions released by muscovite, biotite and hornblende are the main responsible for the increased conductivity in deeper water layers in relation with the surface, which is evidenced by the variation from figure 18.

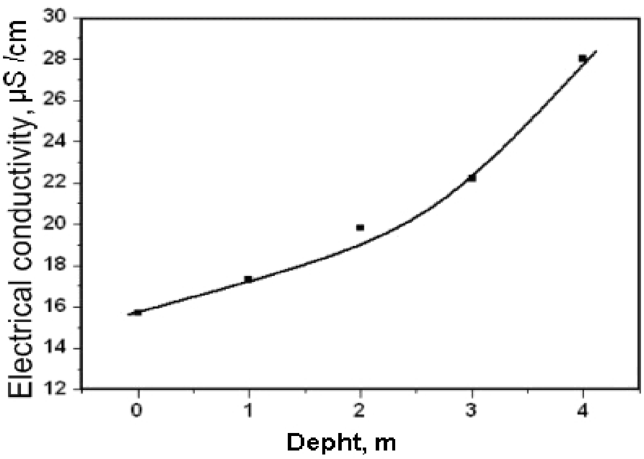


Fig. 18. The variation of electrical conductivity depending on the depth measured in the laboratory, sample from 2010.

Electrical conductivity measurements in situ: Thus, we developed researches that proved fruitful with achievement of a prototype device for measuring in situ RRC 1. In this way we thank to Prof. Dr. Ing Phys. Arghir George, Dr. Ing. Petean Ioan and Ing. Burtescu Andrei for their collaboration in completing this device.

For measuring the electrical conductivity we need two silver electrodes connected to a digital multimeter BT9205A universal type, and for the turbidity measurement an assembly with light emissive diode and a photo resistor as a sensing element. The device is presented in figure 19.

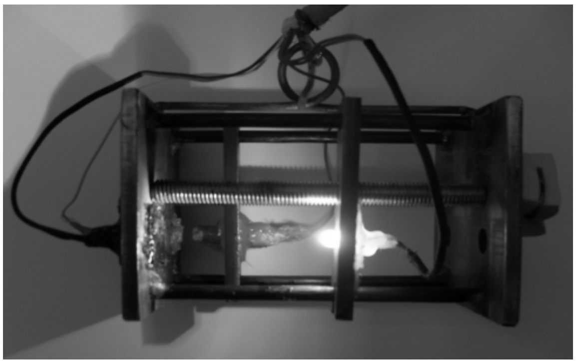


Fig. 19. The prototype in situ measurement of electrical conductivity and turbidity.

One advantage of this method is the much greater number of investigations made exactly on the spot and also the number of experimental points that can better validate a variation. Comparing the results obtained by measurements in situ, we see the same variation of electrical conductivity. The related data are published in an article dealing largely this experience (Câmpean, 2010).

The water turbidity: It is noted that the values obtained are below the limit of 40 NTU, above limit which are starting average turbidity waters. So, in general we can say that the St. Ana Lake has a very low turbidity, as shown in figure 20.

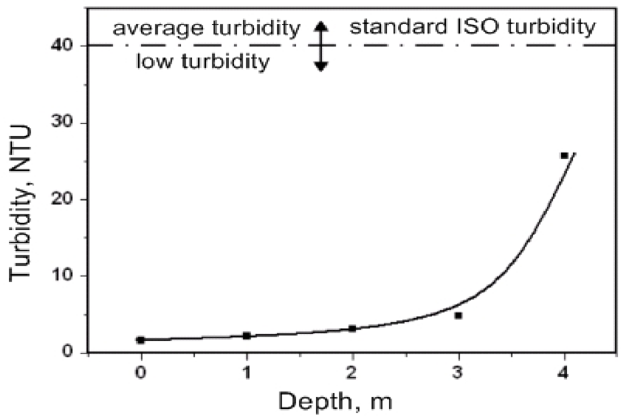


Fig. 20. Turbidity variation measured in the laboratory for water samples in 2010

pH measurement: To determine the water pH are used colorimetric and potentiometric methods. The pH value decreases progressively with the depth, figure 21. That is due to the presence of silicate particles as well as potassium feldspar associated with specific philosilicates as the biotite and the muscovite, showing an acid tendency in the water presence.

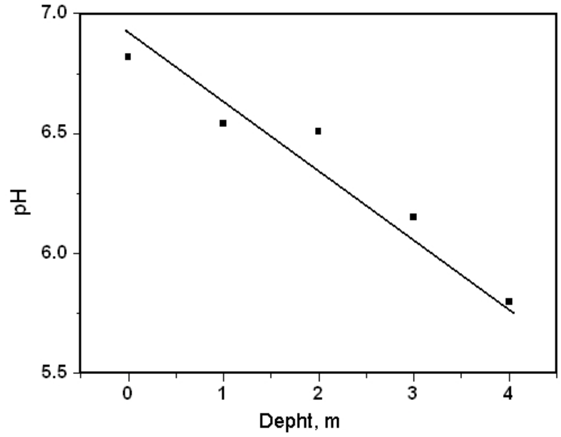


Fig. 21. The pH variation according to depth, samples taken in 2010.

The heavy metals content: Using this modern research method in chemical analyzes it was determined the metal content in water samples taken from St. Ana Lake in August 2010. In that month there were no precipitation reported two weeks before sampling. Were determined the following metals: iron, copper, zinc, lead and cadmium.

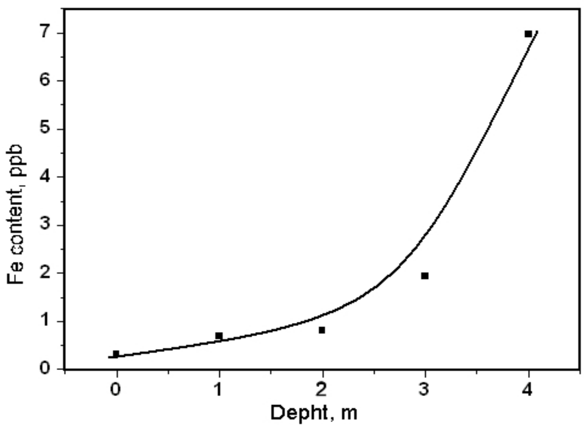


Fig. 22. Fe content variation according to depth, measurements on water samples taken in 2010.

The highest metal content in the water of St. Ana Lake is the iron; in figure 22 we can see a very small amount on the surface but increases rapidly to 3 and respective 4 m depth. That is due to the presence of biotite and hornblende dispersions which released the amount of iron measured. The highest value is 6.96 ppb, a value well below the maximum limit allowed. That itself shows the specific natural environment conservation.

The fact is confirmed by the identification of weak traces of Cu and Zn (Cu = 0.03 ppb and Zn = 0.05 ppb) far below the standard. Therefore, the current measurements in 2010 performed on representative water samples indicate that the St. Ana Lake is in an environmental normal state without obvious signs of pollution. The experimental results obtained in this thesis are in good agreement with published data of Begy et al. 2009, which applied and developed the technique for determining the radioisotope ^{210}Po (^{210}Pb successor) in lake sediment dating by alpha spectroscopy, implementing a dating method for young sediments. For ^{210}Pb concentration the value is 5 Bq / kg.

5.4. Sediments observations on Saint Ana Lake

With the results obtained from measurements at St. Ana Lake we performed a 3D modeling of the lake to highlight the values of the water properties. This is shown in figure 23.

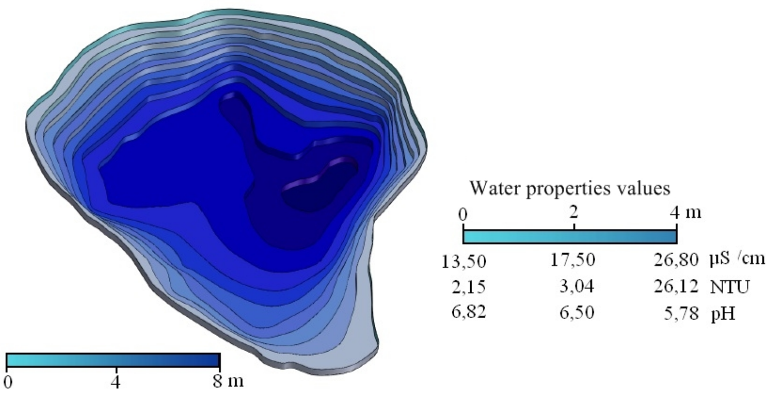


Fig. 23. 3D representation of Saint Ana Lake and the main properties of water distribution

Chapter.VI. Physico-chemical characterization of sediments and suspension specific to salt lakes

The salt deposits in Transylvania are the purest in the world. They were formed by the low water level of the Paratethys Sea in the Badenian in Transylvanian Basin (Peryt, 2006). The most representative deposits are located along the alignment Sovata – Praid and Dej - Cojocna - Turda.

6.1. Experimental research regarding Badenian salt

Sampling and sample preparation of Badenian salt: For this investigation we sampled the high purity Badenian salt from Salina Turda. Salt pieces were ground and a powder was obtained. One part of this powder was used as the reference material and another part was dissolved in ultrapure water 10 g salt in 10 ml water. The resulting solution was laid on a sterile microscope slide and it was monitored under the optical microscope the mineralogical phenomenon of crystallization from solution in homogeneous conditions.

Structural modeling of badenian salt, halite configuration: In our case it is expected that a solution of Badenian salt will help to a homogeneous crystallization instead of a heterogeneous due to its high purity, forming perfect halite crystals. The presence of organic matter and suspended solid minerals salt in a salt solution will help rather a heterogeneous crystallization instead of a homogeneous, case mentioned before (Liu, 2000). First we perform a theoretical crystallographic model for halite crystals for the proper identification of possible forms of crystals and secondly we elaborate the experiment. An aqueous solution 1M of Badenian salt was prepared using pure crystals from the Turda mine. The solution was deposited on a glass microscopic slide in a thin layer and was subjected to natural drying (25 ° C atmospheric pressure) during the investigation of optical microscopy.

Based on FCC elementary cell we have represented in figure 24 the most important crystallographic planes and their properly directions, which are able to help the growth of ideal salt crystals. (Petean et al. 2011)

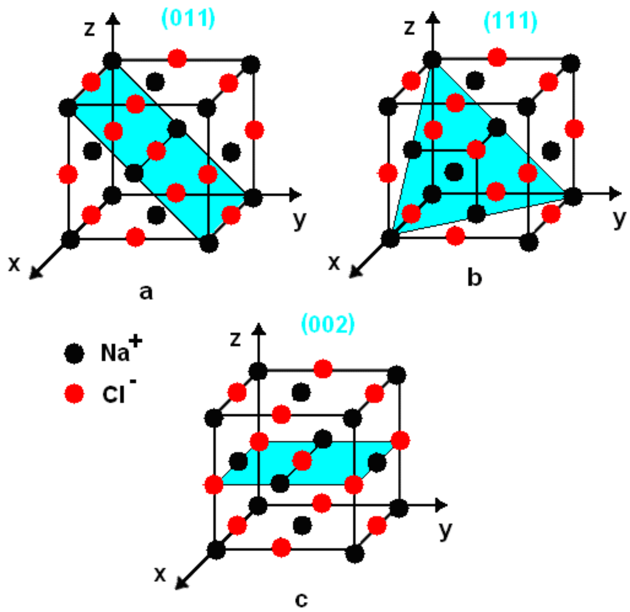


Fig. 24. The evidence of possible crystallographic planes of halite elementary cell. Crystallographic planes: a) {110}, b) {111}, and c) {200}.

Badenian salt crystallization in homogeneous conditions: A sample of Badenian salt and the glass plate with saline solution after complete drying were subjected to X-ray diffraction.

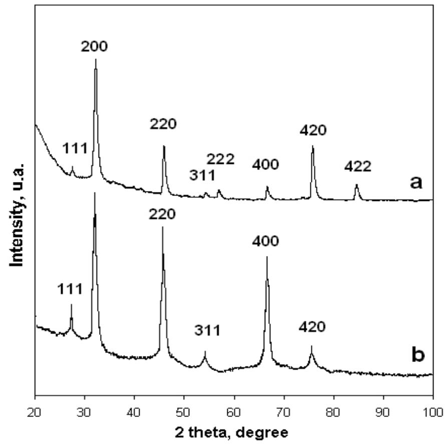


Fig. 25. The diffractograms for: a) powder salt of Badenian b) sodium chloride film completely dry deposited on the microscope slide

figure 25.a represent the X-ray diffraction pattern resulted for the salt powder of Badenian and figure 25. b presents the X-ray pattern resulted for the glass plate of microscope with salt crystals completely dry. In both cases it is observed diffraction peaks well developed related to the crystalline state of salt. The diffraction peaks for salt powder, figure 25.a are a little wider than the peaks observed for the glass surface, figure 25. b, because of the salt particles. On the other hand, the powder crystallizes more crystallographic planes than the microcrystals grown on glass plate. Optical microphotography are obtained on the glass plate after 10 minutes of natural drying, figure 26.

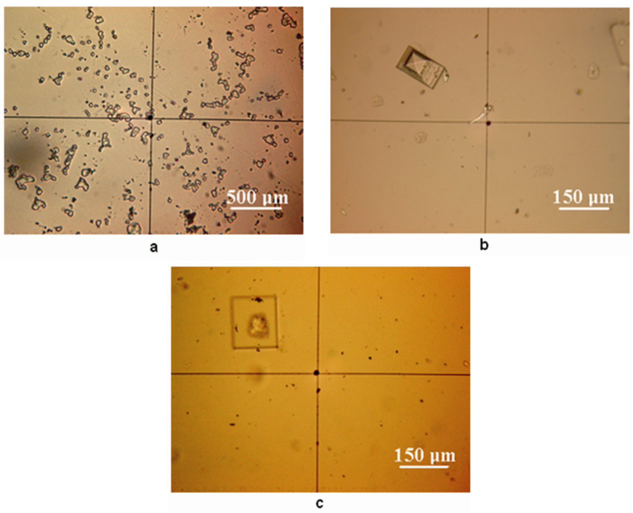


Fig. 26. Optical microphotographs in transmitted light for aqueous solution of sodium chloride after 10 minutes of drying: a) overview of the cluster, b) details of the cluster [110] and c) details of the cluster [200].

Are observed a few clusters of crystal after 10 minutes of drying at lower enlargement, figure 26.a. The clusters are formed due to the gradient concentration caused by water evaporation from the thin film surface of the aqueous salt solution, through homogeneous crystallization.

In figure 27 are presented the optical microphotographs obtained on the glass plate after 20 minutes of natural drying. There are observed crystals strong developed related to a significant decrease of the aqueous salt solution. Are observed a few drops of water and light moisture around the characteristic crystals.

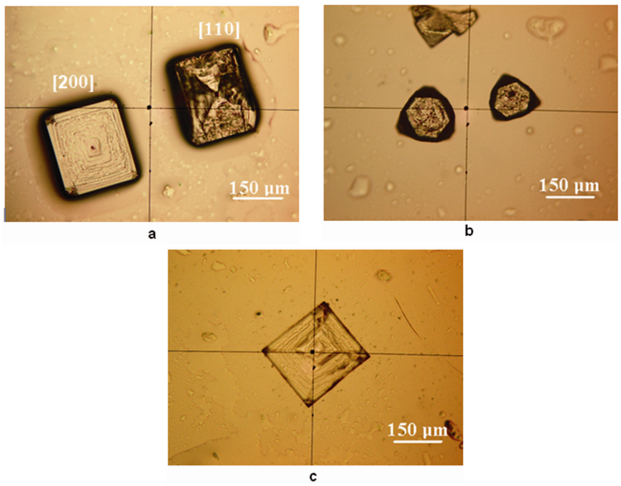


Fig.27. Optical microphotographs in transmitted light for aqueous solution of sodium chloride after 20 minutes of drying: a) the cluster [110], b) details of the cluster [111] and c) details of the cluster [200].

The salt crystals are fully formed after 30 minutes of drying as seen in figure 28. This is evidenced by the lack of moisture and terraces (layers) intermediate on the crystal surface.

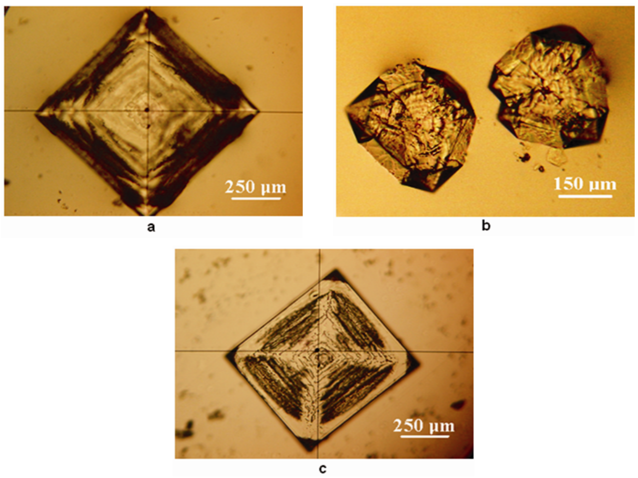


Fig.28. Optical microphotographs in transmitted light for aqueous solution of sodium chloride after 30 minutes of drying: a) the cluster [110], b) details of the cluster [111] and c) details of the cluster [100].

6.2. Investigations on salt lake at Pata Rât

One of the most important alignments of badenian salt deposits of the Transylvanian Basin is Dej - Cojocna - Turda. The presence of salt deposits has a major influence to the topography and the stability of subjected areas. There are reported significant ground movements due to rapid change of conformation of salt deposits which affect the railway embankment Apahida - Câmpia Turzii, Cluj county (Constantinescu, 1996).

Sampling and sample preparation: To reveal these aspects we collected representative samples of soil, water and sludge from a salt lake located on the line Dej - Cojocna - Turda near the town of Cluj - Napoca at Pata Rât. The soil sampled is in the immediate vicinity of the lake, the water sample is taken from the lake surface and the sludge is taken from the lake bottom, figure 29.

a

b

Fig.29. Pata Rât lake , Cluj – Napoca: a) salt deposition of lake bank and b) salt deposits detail on the lake bank and the water mirror

Water and sludge samples were submitted each on a separate glass slide naturally dried. The soil sample was emulsified with deionized water and after was laid on a glass slide a similar uniform layer as consistent with the mud.

Investigation of adjacent soil and water of salt lake: The diffractograms resulted for the soil sample adjacent to the lake and the drop water submitted and evaporated are presented in figure 30. For the soil sample are observed well shaped and slender maximums corresponding to the mineral components of the soil but appear also some less intense and wider corresponding to clay minerals with very fine particles. The resulted diffractogram for the evaporated water presents very well developed and slender maximum corresponding to a mixture of microscopic monocrystals. (Câmpean et al. 2011b)

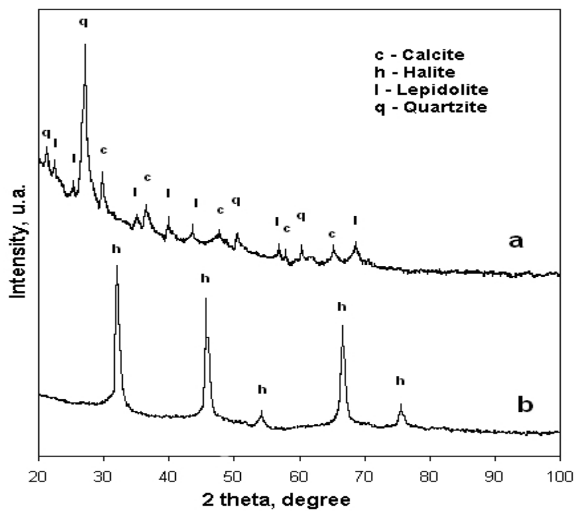


Fig. 30. The resulted diffractograms for: a) soil sample, b) water sample submitted and evaporated.

Investigation of salty sludge: The mineralogical composition of the salt sludge samples collected from salt Lake Pata Rât is shown by X-ray diffraction analysis. The resulted diffractogram is presented in figure 31.

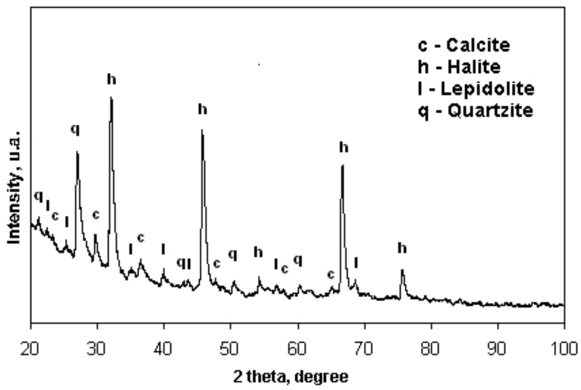


Fig. 31. The representative diffractogram resulting for the salt sludge sample.

The diffractogram from figure 31 has two major overlapping spectra: the resulted spectrum from soil particles and the corresponding spectrum for the crystallized salt. In order of peaks intensity, the most intense is corresponding to sodium chloride.

6.3. Water properties variation in terms of particles in suspension

The microstructural distribution of minerals in water layers: Starting from these premises were taken water samples from surface and from 10 and 20 cm deep, the mud layer being at an average depth of 30 cm.

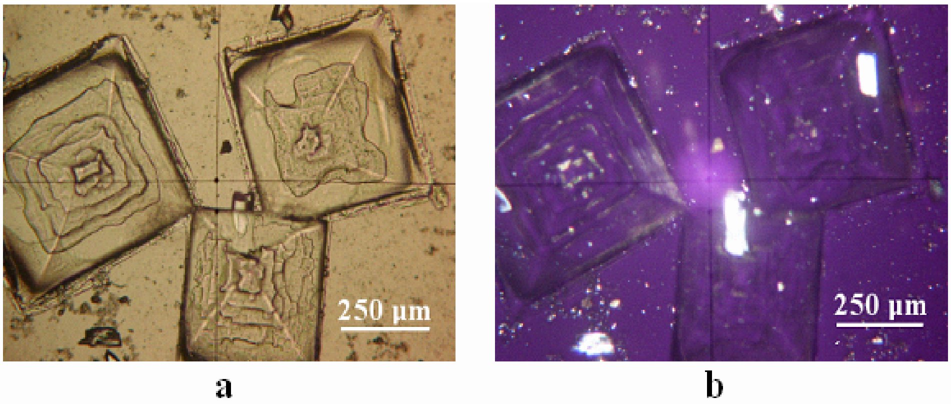


Fig. 32. The optical mineralogical microphotographs for water sample taken from the surface: a) in transmitted light and b) in polarized light with crossed nicols.

The microstructure of a water sample taken from salt lake Pata Rât is shown in figure 32.a. We observe well developed salt crystals after crystallographic directions [110] and [200] joined by material particles of mineral origin. We can see this in polarized light, figure 32.b, salt crystals appearing in translucent blue on the dark background of the image.

At 10 cm depth in figure 33.a. it is shown a salt crystal formed after [200] direction almost visible to the eye (about 1 mm) surrounded by mineral particles from aqueous suspension. That corresponds to a heterogeneous germination promoted by solid inclusions dispersed in saline solution.

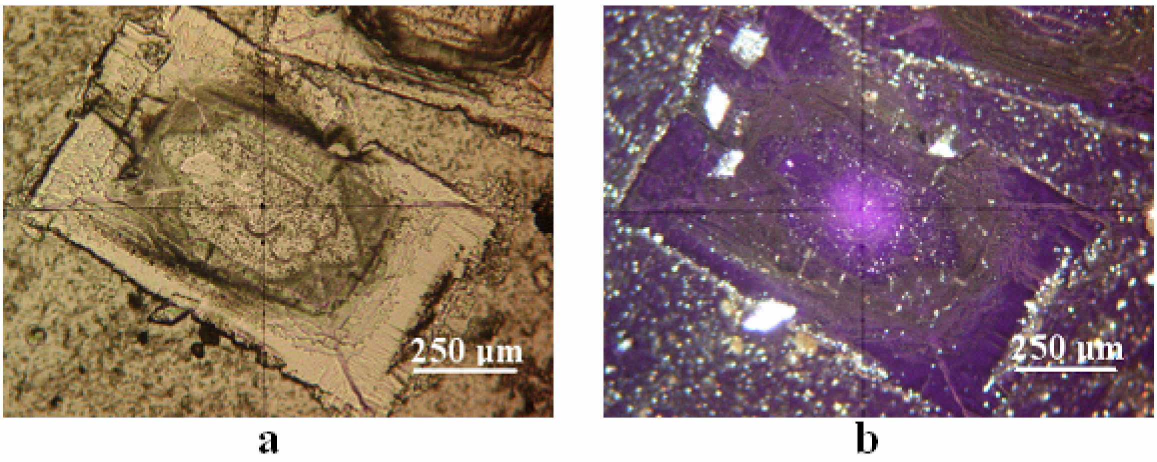


Fig. 33. Optical mineralogical microphotographs for the water sample taken from 10 cm depth: a) in transmitted light and b) in polarized light with crossed nicols.

At 20 cm depth we are very close to the lake bottom, thus, to the incidence of mud area. The optical microscopy in transmitted light shows a halite crystal surrounded by aggregate particles in suspension, figure 34.a. Almost is formed a compact film of material particles from the amount of water exposed on the surface microscopic glass slide. It is obvious the intrusion of these particles inside the halite crystal formed by water evaporation.

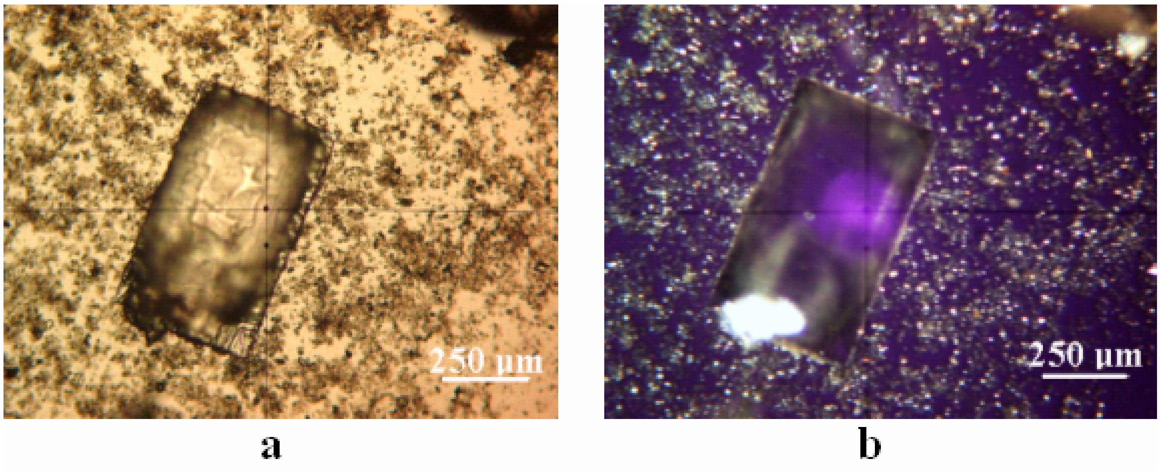


Fig. 34. Optical mineralogical microphotographs for the water sample taken from 20 cm depth: a) in transmitted light and b) in polarized light with crossed nicols.

In polarized light with crossed nicols, figure 34.b, it is observed the main of quartz particles (gray green) associated with calcite (brown yellow) closely surrounded by very fine brown pink lepidolitics particles and bright white kaolinitic particles.

The threedimensional microphotography in dark field for water sample taken from 20 cm depth is shown in figure 35. This highlights the mineral particles embedded in formed halite crystal mass.

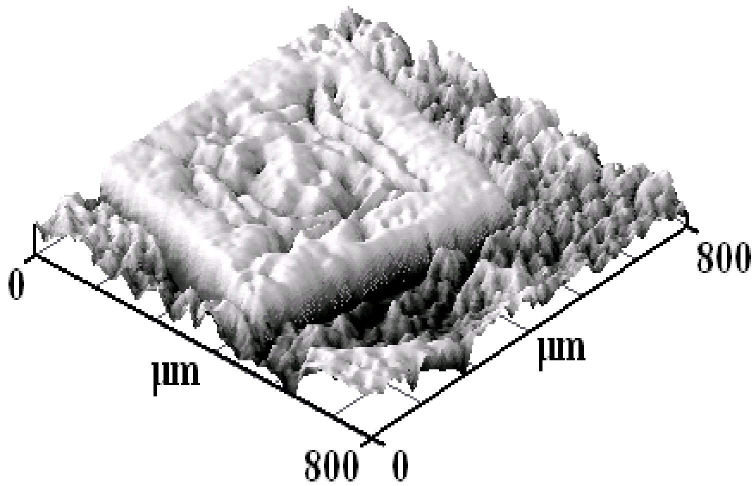


Fig. 35. Optical microscopy in dark field - three-dimensional representation of a water sample taken from 20 cm depth and dryed on the glass slide.

Variation of electrical conductivity: Observing the values of electrical conductivity at different investigated depths, figure 36 shows an almost linear decrease of it in relation to lake depth.

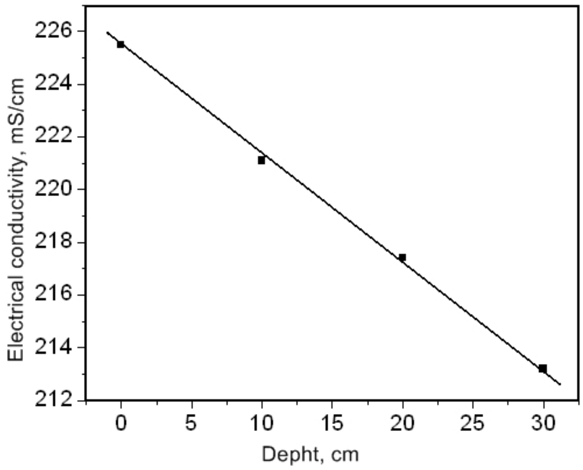


Fig. 36. Variation of electrical conductivity of water samples from the Pata Rât according to depth.

pH variation: We see in figure 37 that the pH varies almost exponentially with water sampling depth, respectively with the input of revealed particulate matter.

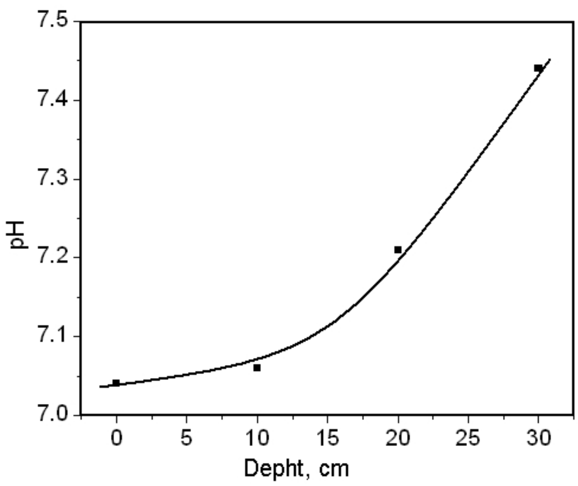


Fig. 37. Variation of water samples pH from Pata Rât according to depth.

An explanation of this variation is possible if we consider the alkaline contribution of calcite particles in direct contact with the lake water. The pH tendency is to grow in the presence of water mineral suspensions.

Chapter.VII. Conclusions and personal contributions

The investigation of sediments in aqueous suspension in different limnological systems is an interesting research area specific to physical environment. The different physical or chemical conditions are found intermingling with geological and hydrological formations in a given region, which leads to the formation of specific limnological systems.

The literature study shape the fundamental geological aspects of the Transylvanian Basin, due to large fluctuations of Paratethys Sea. The analyses performed indicate a very high purity of these salt deposits, being composed almost entirely of sodium chloride.

The eastern border of the Transylvanian Basin is bordered by the eastern side of the Eastern Carpathians, with significant volcanic features, including Great Ciomadu Massive. The specific minerals of this volcanic edifice were identified as follows: potassium feldspar, potassium hornblende, biotite, potassium muscovite, potassium silicate hydrate embedded in an amorphous mass of andesite.

The geological diversity for Transylvanian Basin leads at the formation of specific limnological and various systems as:

- salt lakes formed in the salt areas, such Dej - Turda, Sovata, Praid;
- the only volcanic crater lake in southeastern Europe - St. Ana Lake located in Mountain Ciomadu Mare in Harghita county.

The original contributions of the thesis focus on the investigation of two case studies with clear features. The first relates to the volcanic crater St. Ana Lake because is the only limnological system of this kind in this part of Europe and the second is the salt lake Pata Rât.

A personal contribution is to identify the mineral components of powder materials of the shore of St. Ana Lake, able to form suspensions in water also and their distribution. The shore soil of the St. Ana Lake is sized in three categories of particles: coarse gravel, fine gravel and sand. Their analysis shows that they are composed of potassium feldspar, potassium hornblende, biotite, potassium muscovite, potassium silicate hydrate embedded in an amorphous andesite mass.

The identified minerals correspond in terms of source area to the exposed layer at the geological formations surface of that area and are according with published data. Of these particle categories only the sand and the dust are likely to lead to the formation of sediments in aqueous suspension due to the presence of microscopic particles in a wide range from 3 to 250 μm.

We showed the distribution of suspended particles in the different layers of water and highlight their nannostructure and microstructure. The distributions obtained are likely to correlate with water properties variation and to explain it. The minerals with the highest susceptibility to be found in aqueous suspension are the muscovite, and in the smallest is the hornblende. That is sustained by the similar composition resulted for the sludge sample from the bottom lake. The only difference is that it has a range of microscopic particles much finer, about 1 - 50 µm average diameter.

We developed a physical geometric sedimentary model considering the tabular lamellar particles morphology (biotite, muscovite, hornblende) called the "tabular model". The tabular model developed for this clay type particles, confirms the assumptions because the microscopic particles weight (1 - 3 µm diameter) is of the order of micro-Newton, force smaller than the surface interactions of colloidal type, which occur in relation to lake water. The water samples taken along three years of research have been analyzed in terms of particle dispersion, the result being a concentration of material nanoparticles in the surface layers of lake up to 2 m depth, while the microscopic particles are found at 2 m down especially close to the mud layer. This stratification of particulate matter pleads for their immobilization in water layers during the water streams which are feeding the lake with water due to their small size. That is according with literature which mentions that in the St. Ana Lake is not found thermal stratification due to its reduced depth. The bathymetric measurements indicate an average ceiling of the bottom lake at 4 m depth. At the maximum area depth are 7 - 8 m measured.

The particulate matter distribution in suspension in the different layers of water is likely to influence the water properties. A new element and a personal contribution is the design a device for in situ measurement of water conductivity and turbidity based on rezistometrics sensors. Therefore there is a progressive turbidity increase with the water layer depth but without coming into the murky water, the values are below the limit value of 40 NTU.

Although the identified minerals are not dissolved in water, some of them such as biotite, hornblende and muscovite in prolonged contact with the water may release ions such as those of iron, which determine the electrical conductivity variations of water. That is supported by iron levels determined in different layers of water which increases as depth increases.

The presence of clay minerals in aqueous suspension is likely to release ions such as K, Al, Fe, which increases the electrical conductivity of water layers with deep, and by the increasing of particles density in suspension.

The presence of these mineral particles from pyroclastites is likely to induce a lightly acid pH of water, which is observed by lowering the water pH from the normal value for rainwater to low sensitive values.

Were performed AAS analyzes in laboratory to determine the content of heavy metals such as Pb, Cd, Hg, Zn and Cu. It was found traces of Cu and Zn but well below of the standard and this come from joined elements of piroclastites which are underlying the volcanic cone. The lead and cadmium levels determined in 2010 for the water samples are undetectable. That indicates a normal situation in terms of the environment in 2009, 2010, compared with some literature data which for 2008 signaled significant advanced values for Pb and Cu in surface layers.

Was also measured the Fe content in successive water layers because the Fe ions are released from biotite and hornblende particles in suspension. The results show an increase of Fe content with water layers depth, increases proportional with the density of suspended particles in the respective layer.

The Transylvanian Basin is characterized by salt bearing beds of Badenian that interfere with water supplies forming ponds and some salt lakes. The Pata Rât Lake is part of the salt bearing bed Dej - Turda - Cojocna, where the interaction of very concentrated salt water with the soil, forms a thin layer of salt mud. The investigations reveal the formation of soil with calcite particles mixed with large amounts of fine particles of lepidolite with 5 5 µm diameter.

The soil particles are embedded in a very salt water showing aquatic vegetation traces which are forming a dense jellied mud. In dry state the thin film mud reveals large halite crystals oriented in the [110] direction and rarely on the [111] direction. The composition revealed by the salt mud from Pata Rât proves to be suitable for SPA therapy for skin and rheumatic complementary treatment.

From the investigation it appears that the interrelation soil - water - salt deposits underlying the formation of salt lakes in Transylvanian Basin. Their formation mechanism works only with these three elements related to a whole active, able to influence the geological disposal of the soil.

The performed analyzes show a high solubility of sodium chloride in water, quickly forming a saturated solution in contact with saliferous underground massive. I noticed that the water evaporation of such natural brine, leads to the formation of microscopic crystals of halite. That in itself shows a relative importance, if it is assessed separately, being extremely useful for salifer exploitation by “Solvay” method, where the deep salt is extracted through a saturated brine.

For the salt Pata Rât Lake was revealed the close relationship between massive salt and sediment above them, mediated by the presence of springs and deep water layers. As previously mentioned, these analyzes revealed in them large amounts of calcite rocks mixed with large clay and sand-clay deposits (muscovite, kaolinite, lepidolit mixed with quartz sand and / or calcite).

Another personal contribution in this direction is the physico-chemical characterization of specific sediments of Transylvanian Basin and their interaction with salt water. Thus, we modeled the crystallization of sodium chloride in homogeneous conditions and we investigated from morphological and structural point of view the specific mud of salt Lake Pata Rât. The analyzes on representative samples of mud from the Pata Rât lake shows that it consists of a fine paste naturally matured. The basic texture is composed of clay particles (lepidolit) with average diameters between 1 and 5 µm which are connected with salt water in colloidal type micelles. In this natural matured paste, occur traces of microscopic algae specific to salt water and a range of fine particles such as quartz and calcite with average diameters around 25 µm.

The physical and mineralogical characteristics of this mud specific to the Pata Rât salt lake is suitable for use in alternative treatments for rheumatism and skin exfoliation treatments.

Chapter.VIII. Selected Bibliography

1. Alexe M., Şerban Gh., 2006: Rolul gis şi gps în managementul zonelor de dizolvare pe diapir - studiu de caz: lacurile sărate de la Sovata, Geographia Technica , No. 1.
2. Arghir G., Ghergari M. L., 1986: Cristalografie – Mineralogie, Litografia Universităţii Tehnice din Cluj – Napoca. 382p.
3. Arthur S., 2006: Arealele salifere de pe valea Mureşului, amonte de Reghin, Colocviul de etnografie "Interferenţe cultural - etnice" - Muzeul etnografic Reghin.
4. Balla Z., 1987: Tertiary paleomagnetic data for the Carpatho-Pannonian region in the light of Miocene rotation kinematics. Tectonophysics 139, 67–98.
5. Baselt D., 1993: The tip-sample interaction in atomic force microscopy and its implications for biological applications, General concept and defining characteristics of AFM, Ph.D. thesis, California Institute of Technology.
6. Begy Robert-Csaba, 2009: „Studii de mediu prin utilizarea radioizotopului ^{210}Pb”, Teză de doctorat, Universitatea „Babeş Bolyai” Cluj-Napoca, Facultatea de Ştiinţa Mediului, conducător ştiinţific Prof. univ. dr. Constantin Cosma, pp. 116-124.

7. **Câmpean R. F.,** Ristoiu D., Arghir G., 2009a: Carbonated-Clay Ground Deposits Potential Natural Sources of Atmospheric Pollution with Material Particles, International Conference Environment & Progress, Cluj – Napoca 2009, Abstract book, pag. 29.
8. **Câmpean R. F.**, Ristoiu D., Arghir G., 2009b: Aspects Concerning the Nano - Sediments Compozition and Distribution in St. Ana Lake – Romania, Studia Universitatis Babes – Bolyai Ambientum, LIV, 1 – 2, p. 11-19.
9. **Câmpean Ramona Flavia,** Arghir George, Petean Ioan, Ristoiu Dumitru, 2009c: Adaptarea regimului de difracţie cu raze X pentru identificarea fazelor din nisipul de pe malul lacului Sf. Ana, Ştiinţa şi Inginerie, vol. XVI, Editura AGIR, Bucureşti, , ISBN 978-973-720-246-8, pag. 259 – 266.
10. **Câmpean R.F.,** Petean I., Arghir G., Burtescu A., 2010: In Situ Measurement of Water Electrical Conductivity and Turbidity For St. Ana Lake – Romania, Acta Technica Napocensis Series: Matematica Aplicata si Mecanica, 53 (III), p. 533 -538.
11. **Câmpean R.F.,** Olah N. K., Toma C., Ristoiu D., Arghir G., 2011: In Depth Variation of Water Properties For St. Ana Lake – Romania Related to Sediments in Suspension, Studia Universitatis Babes – Bolyai Chemia, LVI, 1, p.107 – 117.
12. **Ramona Flavia Câmpean**, Alexandra Gertrud Hosu Prack, Ioan Petean, George Arghir, Dumitru Ristoiu, 2011 b: Consideraţii mineralogice privind lacurile sărate din badenian situate în Podişul Transilvaniei, Ecotera, 26, p. 17 – 20.
13. **Câmpean R.F.,** Petean I., Bărăian M., Gertrud Hosu Prack A., Ristoiu D., Arghir G., 2012: Mineral Particullate Matter from the St. Ana Lake sand Related to the Water Suspensions, Carpathian Journal of Earth and Environmental Sciences, vol. 7, nr.2, p. 57 – 66.
14. Ciupagea D., Paucă M., Ichtim T., 1970: Geologia Bazinul Transilvaniei. Ed. Academiei Române, 256 p., Bucureşti.
15. Codrea V., Dica P., 2005: Upper Cretaceous-lowermost Miocene lithostratigraphic units exposed in Alba Iulia-Sebeş-Vinţu de Jos area (SW Transylvanian basin). Studia Universitatis Babeş-Bolyai, Geologia, 50 (1-2): 19-26, Cluj-Napoca.
16. Codrea V., Hosu Al., 2001: The Paleocene-Eocene formations and the Eocene-Oligocene boundary in the Jibou Area (Sălaj country). Field Trip Guide, 4th Regional Meeting of IFAA, 93-107, Cluj-Napoca.
17. Constantinescu E., Matei L., 1996: Mineralogie determinativa, Ed. Universitatii din Bucuresti, Bucuresti.
18. Csontos L., Nagymarosi A., Horváth F., Kovac M., 1992: Tertiary evolution of the Intra-Carpathian area: a model. Tectonophysics 208, 221–241.
19. Csontos L., 1995: Tertiary tectonic evolution of the Intra-Carpathian area: a review. Acta Vulcanol. 7 (2), 1–13.
20. Duborg F., Aime J.,P., 2000: Role of the adhesion between a nanotip and a soft material in tapping mode AFM, Surface Science 466, p. 137–143.
21. Filipescu S., 1997: Several comments on the nomenclature of the lithographic units from the Transylvanian Basin, Studia Univ. Babeş-Bolyai, Geologia, XLII, 2, Cluj-Napoca.
22. Filipescu S., 2001: Cenozoic lithographic units in Transylvania. Field Trip Guide, 4th Regional Meeting of IFAA, 75-92, Cluj-Napoca.
23. Filipescu S., Kaminski M., 2008: Paleogene Deep-water Agglutinated Foraminifera, in the Transylvanian Basin. In Kaminski, M. A., Coccioni, R., Marsili, A. (eds.), Proceedings of the Seventh International

Workshop on Agglutinated Foraminifera, pp. 25-30. Grzybowski Foundation Special Publication, London.

24. Filipescu S., 2005: Revizuirea semnificaţiei şi conţinutului unităţilor litostratigrafice din Neogenul Bazinul Transilvaniei conform recomandărilor şi standardelor Comisiei Internationale de Stratigrafie, Raport de cercetare, Revista de Politica Ştiinţei şi Scientometrie - Numar Special - ISSN- 1582-1218.
25. Gâştescu P., 1971: Lacurile din România, Limnologie regională, Ed. Academiei, R.S.R., Bucureşti, 372 p.
26. Gheerbrant E., Codrea V., Hosu Al., Sen S., Guernet C., Lapparent de Broin Fr., Riveline J., 1999: Découverte de vertèbres dans les Calcaires de Rona (Thanetien ou Sparnacien), Transylvanie, Roumanie: les plus anciens mammiferes cenozoiques d'Europe Orientale Eclogae geol. Helv. 92 (1999): p. 517-535, Basel.
27. Hosu A., 1999: Arhitectura sedimentaţiei depozitelor Eocene din nord-vestul Bazinul Transilvaniei, Ed. Presa Universitară Clujeană, 224 p, Cluj-Napoca.
28. Huismans R.S., Bertotti G., Ciulavu D., Sanders C.A.E., Cloetingh S., Dinu C., 1997: Structural evolution of the Transylvanian Basin (Romania): a sedimentary basin in the bend zone of the Carpathians, Tectonophysics, 272, , p. 249-268.
29. Juvigne E., Gewelt M., Gilot E., Hurtgen C., Seghedi I., Szakacs A., Gabris Gy., Hadnagy A., Horváth E, 1994: Une éruption vieille d'environ 10.700 ans (^{14}C) dans les Carpates orientales (Roumanie). Isotopic Geochemistry. Comptes rendus de l'Academie des sciences, Paris 318: 1233–1238.
30. Kovacs H. M., Ristoiu D., 2009a: Uptake of persistent organic pollutants by vegetables grown in contaminated soil in Cluj district, Romania, Epidemiology, 20 (6), p. 66.
31. Kovacs H. M., Ristoiu, D., 2009b: Optimization of methods for the determination of disinfection byproducts in drinking water. Studia Chemia, 4 (1), p. 143-149.
32. Magyari E., Buczko K., Jakab G., Braun M., Szanto Zs., Molnar M., Pak Z., Karatson D., 2006: Holocene paleohydrology and environmental history in the South Harghita Mountains, Romania, Foldtani Kozloni, 13, 249-284.
33. Moriya I., Okuno M., Nakamura T., Ono K., Szakacs A., Seghedi I., 1996: Radiocarbon ages of charcoal fragments from the pumice flow deposit of the last eruption of Ciomadul volcano, Romania. Summaries of Researches using AMS at Nagoya University 7, p. 255.
34. Ioan Petean, George Arghir, **Ramona Flavia Câmpean**, Marius Bărăian, Alexandra Gertrud Hosu Prack, 2011: Crystalographyc relations applied to homogeneous cristalization of badenian salt, Acta Technica Napocensis Series: Matematica Aplicata si Mecanica, 54 (I), p. 193 – 200, ISSN 1221-5872.
35. Peryt M., 2006: The beginning, development and termination of the Middle Miocene Badenian sa linity crisis in Central Paratethys. Sediment. Geol., 188–189: 379–396.
36. Pilbath A.G., Pal Z., 2007: Microregiunea Ciomad-Balvanyos, Ed. Green Steps România, 116 p.
37. Proust J.N., Hosu A., 1994: Tectono-stratigraphic significance of the paleogene reds beds in the Transilvanian Basin. Studia Universitatis Babeş-Bolyai Geologia, 39 ½, 33-60.
38. Rickwood P.C., 1981: The larger crystals, American Mineralogist, 66, p. 885 -907.
39. Ristoiu D., Cosma C., Voros A., Ristoiu T., 1998: Evaluation of the volatile organic contents in aqueous samples by HI-QMS technique, Vacuum, 50, 3-4, p.359-362.

40. Ristoiu D., von Gunten U., Mocan A., Chira R., Siegfried B., Kovacs H. M., Vancea S., 2009: Trihalomethanes formation during water disinfection in four water supplies in the Somes river basin in Romania. Environmental science and pollutants research, 16, p. 55-65.
41. Rusu A., 1970: Corelarea faciesurilor Oligocenului din regiunea Treznea-Bizuşa. Şt. Geol. Geol., 15/2: 513-519, Bucureşti.
42. Rusu A., 1989: Problems of correlation and nomenclature concerning the Oligocene formations in NW Transylvania. The Oligocene from the Transylvanian Basin, 67-78, Cluj-Napoca.
43. Seghedi I., Szakács A., Snelling N. J., Pécsay Z, 2004 b: Evolution of the Neogene Gurghiu mountains volcanic range (East Carpathians, Romania), based on K-AR geochronology. Geologica Carpathica 55, 325-332.
44. Stark M., Moller C., Muller D. J., Guckenberger R., 2001: From Images to Interactions: High-Resolution Phase Imaging in Tapping – Mode Atomic Force Microscopy, Biophysical Journal, 80, p. 3009-3018.
45. Wiesendanger R., 1994: Scanning Probe Microscopy and Spectroscopy.Methods and Applications. Cambridge University Press.
46. Zorn I., 2004: Ostracorda from lower Badenian (Middle Miocene) grund formation (Mollase Bazin, Lower Austria), Geologica Carpatica, apr., pag. 179 – 189.