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## CRYSTALLINE FORMATIONS IN CENTRAL REGION OF THE DNIESTER RIVER BASIN

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**Abstract:** In the central region of the Dniester River Basin – the NNE part of the Republic of Moldova - petrological studies have been carried out in order to detail the lithology of the crystalline rock complexes, to assess their origin and the prospecting areas with possible ore accumulations. These crystalline rocks are Archean to early Proterozoic in age and can be divided into several formations: Gneisses formation (upper Archean), Enderbites formation (upper Archean – early Proterozoic), Alaskites formation (early Proterozoic) Metasomatites formation, Dinamomorfites formation. Concentrations of La and Ce have been detected, exceeding the geochemical background. Probably significant accumulation of REE can be found in the basal layers of platform sedimentary cover in detrital aureoles consisting of zircon and monazite - the main sources of REE in this area.

**Keywords:** metamorphism, ultrametamorphism, metasomatism, geological formations, zircon, monazite, REE.

### I. Introduction

During the second half of the last century, in the north-east of the Republic of Moldova, the study of the structure and geological evolution of the crystalline formations, covered by a much younger complex sedimentary cover were carried out (Geru, 1987). Economically, this study solves the problem of location in space of the areas most promising for precious metals deposits, REE, radioactive elements and zirconium (Lvina, 1972).

The study of the crystalline successions, mostly Archean and early Proterozoic, that make up the basement of the investigated area, poses many difficulties, being a permanent subject of debate. The formations of the crystalline basement from the middle part of the Dniester River are constituted of rocks composed largely of variable ratios of the same minerals; therefore, their stratigraphic sequence is often arbitrary. For example, some metamorphic varieties can be separated only based on auxiliary criteria: accessory minerals, presence or absence of specific geochemical aureole, petrophysical properties etc. Other rocks, frequently found in zones of metasomatic processes also have similar features.

### II. Geological background

The study of the crystalline rocks, in most cases of Archean and early Proterozoic age, located in the crystalline basement, was and remains a difficult problem and presents a topic of permanent discussion. Crystalline basement formations from central region of Dniester River basin are constituted of rocks with almost similar mineralogical composition, and, on this account, stratigraphic sequence can be tackled in an arbitrary way. For example, some metamorphic varieties differ from each other only on the basis of auxiliary indexes - accessories mineralization, the presence or absence of specific geochemical aureoles, petrophysical properties, etc. Other rocks, frequently found in the regions affected by metasomatic processes, have similar characteristic features.

In the central region of the Dniester River basin, crystalline rocks of basement can be divided into several formations, which differ from one another by petrographic compositions, age and origin: Gneisses formation (upper Archean), Enderbites formation (upper Archean - lower Proterozoic), Alaskites formation (lower Proterozoic) Metasomatites formation, Dinamomorfites formation (Zaharov et al., 1987). The main geological - structural element in the north – eastern part of Republic of Moldova is presented by *Dniester Fault*. In many publications, this area appears under the name of "*Dniester Aulacogen*", which also emphasizes the structural graben aspect of this area.

### III. Petrography

**1. Gneisses formation.** The most important feature of Gneisses formation is the polyfacial character of all rock varieties and it is of note that the progressive and retrogressive metamorphic processes throughout the area took place at different times.

The main minerals, usually biotite - pyroxene - amphibole – plagioclase, show broad variation of their proportion in rocks; accessory minerals are represented by garnet, cordierite, apatite, zircon, ilmenite, and magnetite.

The mineralogical and chemical composition of the rocks from gneisses formation corresponds with metamorphic rocks with a low content of SiO<sub>2</sub> (crystalline schist) and rocks containing normal or saturated with SiO<sub>2</sub> (gneisses).

**2. Enderbites formation.** Some researchers include the enderbites in a general formation known as the charnockites formation (Dmitrov, 1977). Local geologists, examining enderbites only in relation with the rocks rich in sodium, highlight enderbites formation as an independent unit.

Specific features of the enderbites formation in Dniester River region are:

- Presence only in early Precambrian formations;
- Associative relations with crystalline schists or hypersthene gneisses;
- Structural relations concordant with host rocks (crystalline schists and gneisses);
- Variable mineralogical composition, characterized by broad modal variation of each individual component;
- Various grain size; variability of structures and textures, some of which are specific of igneous rocks.

In the central zone of the Dniester River basin the enderbites formation contains the following rocks: enderbites (including cordierite enderbites) plagiogranite (biotite, with garnet, with cordierite), plagiomigmatite (biotite, pyroxene, with garnet, with cordierite), plagiopegmatite (including plagiopegmatite with hypersthene), pyroxenite and pyroxene amphibolite, gabbro-norite. These are genetically related to the earliest metamorphic formations, are characterized by a relatively high sodium content (Na<sub>2</sub>O 4,3-5,4%), have specific structural features and textural and mineral associations of different origins and ages.

In terms of mineralogical composition, the rocks in the enderbites formation are quite varied, but all have relatively high concentrations of plagioclase with oligoclase to andesine compositions (An<sub>25-40</sub>), which makes up most of the rock mass. Beside hypersthene, in rare occasions, another monoclinic pyroxene may be present - green diopside with pale shade, which practically makes it difficult to distinguish from hypersthene in hand specimens.

Separate bands enriched in accessory minerals (magnetite and apatite), are present together with chlorite and biotite in areas with poor cohesion between plagioclase and quartz crystals or in rock fissures. Magnetite has the average content of about 3000 g / t, and apatite – the average is approximately 500 g / t; other accessory minerals (garnet, monazite and zircon) are present in small quantities. At the same time, in some biotite - plagiogranite, the concentration of zircon is 331 g / t, monazite - 211 g / t, garnet - 20 759 g / t. Some rocks of the formation contain ilmenite in relatively low concentrations.

**3. Alaskites formation.** Rock varieties of alaskites formation - alaskites, leucogranites, and granodiorites (pure or garnet-bearing) are most commonly found in the Dniester river basin region in comparison with other formations of crystalline basement; they form quite thick sequences. Alaskite bodies are relatively diverse and are represented by veins, lenses, thin inclusions in gneiss or charnockitoides, zones with xenoliths of older rocks or extended zones homogeneous in terms of their petrography. Some pegmatoides or metasomatic rocks are also present in the alaskite formation.

The place of alaskites formation in the sequence of the crystalline basement is determined by geological processes in the final stages of cratonization, which manifested by ultrametamorphism of earliest rocks from gneisses formation and of relatively young rock of enderbites formation. Simultaneously, a silicic - potassic metasomatism process took place, which have led to the formation of microcline granite varieties.

In the rocks of the alaskite formation, the paragenetic associations are relatively simple and differ from one another only in general mutual relations (structural and quantitative) of the main minerals - potassium feldspars (microcline) and plagioclases (An<sub>20-30</sub>, lacking polysynthetic twinning). Rocks with garnet and cordierite also occur in this formation. Apart from alaskites – leucogranites, some rocks of pneumatolitic - metasomatic origin were identified as pegmatoides.

Unlike enderbites, in alaskites, the quartz is present in two modifications - "foreign" quartz brought from other areas of the background, and quartz deposited during granitoids formation.

Most rocks of the alaskite formation are distinguished by their typical porphyroblasts. Porphyroblasts composed of plagioclase and microcline occur in a fine-grained mass with feldspathic

composition. At the same time, some varieties of alaskites are distinguished by hypidiomorphic granular structure.

In terms of chemical composition, the rocks of the alaskites formation are relatively homogeneous. High concentrations of  $\text{SiO}_2$  in rocks: 74 % alaskite, 72 % leucogranite, and 71% in migmatite is explained by the action of silica flux brought from other areas of the underground.

If we compare the associations of accessory minerals of rocks from alaskites formation with the gneisses and enderbites formations we find the same assemblages consisting of magnetite, zircon, monazite, apatite and garnet. Zircon and monazite concentrations in granitoids formation can be quite high. In some varieties is observed a high concentration of garnet, which can become a major mineral. It is possible that the accessory minerals are not genetically related to their actual host rocks, being inherited from some protoliths.

Most varieties of crystalline rocks in alaskites formation composition contain magnetite; its relatively high concentrations were detected in some wells and due to metasomatic processes occurred in the final stages of formation establishment.

**4. Metasomatites and dinamomorfites formations.** The regions of metasomatic processes in the central region of the Dniester river basin related to disjunctive tectonics orientated to the north-west and north-east directions or with some geological boundaries, which demarcate the rock formations. These rocks are located mostly in tectonic areas with weak cohesion; metasomatites are in spatial correlation with dinamomorfites; often metasomatic rocks and dinamomorfites are indivisible.

Majority of metasomatic formations are characterized by a complex zonality, reflecting a regular event of the process. Since the beginning is formed specific products of iron - magnesium metasomatism, then potassium, and in the final stages - silica. Usually, in the final stage of metasomatism enriching material space with quartz and simultaneously, reduces the concentration of accessories minerals in the rock.

Because of the complex mineralogical composition, metasomatites systematization poses many difficulties. All granitization cycles that took place in the slope region of Ukrainian Crystalline Shield, including the middle zone of Dniester River basin, were achieved by a metasomatic process that introduced plagioclase in the composition of enderbites formation and pegmatoids in alaskites formation.

In active tectonic regions, during long geological periods, metasomatites are in genetic relations with tectonic breccia, cataclasites and milonites from faults zones; called by many geologists rocks of dynamic stress, highlighting the variety of stress granite, stress enderbite, etc. (Geru, 1987). Injection of high-temperature fluid solutions in falling-out areas generated a very complex rocks variety. The compositional variations of the metasomatites in those areas was induced by the combined effect of the fluids and the composition of the original rocks.

A special feature of calcium - magnesium - iron metasomatism from the study area is manifested by the formation of so-called calciphyre, in the composition of which, in addition to calcite (> 95%) are also present pyroxenes.

#### **IV Premises of prospecting for rare earth elements**

In the research done by several generations of Moldavian geologists within the territory of the Republic of Moldova, namely in the central region of the Dniester river basin - northern and north-eastern part of the republic, in geological formations at depths of 50-400 m, mineralizations of zircon, monazite, xenotime and coffinite were detected. Based on spectrographic analysis in different petrologic varieties of the crystalline basement and terrigenous layers situated in the deposit directly on the aureoles of REE of the crystalline basement, with quite high concentrations were determined. Thus, in granitoides of alaskites maximum concentrations of Lanthanum reach about 120 g / t and Cerium - 80 g / t.

The local sedimentary concentration of REE, significantly exceeding their contents in the source rocks, is related to the presence of monazite and zircon. Remarking the high correlation coefficient between zircon and monazite ( $\rho = 0.73$ ), and satisfactory degree of correlation ( $\eta = 8.6 > 3$ ) (Popuiac, 2013), we can assume that these two minerals, in terms of geology, are syngenetic, and probably, as accessory minerals, were formed simultaneously in the same petrologic formation (Zaharov et al., 1987). At the same time, analyzing mineralogical data of the crystalline formations mentioned above, it is determined that monazite, unlike zircon, occurs later in the sequence, i.e. zircon is present in practically all rock types, including those of Archean age, while monazite occurs in rocks of early Proterozoic age.

REE concentrations in crystalline rocks, are generally insignificant. According to some researchers, relatively high concentrations of these elements, which would present a practical interest, can be found in the basal layers of platform sedimentary cover, where were discovered relatively high amounts of monazite( from 5.0 to 10.2 kg / t) and zircon (from 4.9 to 13.4 kg / t), products of the disintegration of the crystalline basement rocks. In almost all mineralogical samples, a fairly stable relation was observed, with zircon concentration exceeding monazite concentration. Nevertheless, the results of the spectrographic analyses, showed that the REE in the monazite fraction may be higher than in the zircon fraction. In areas with significant zircon and monazite mineralization, the concentrations of cerium and lanthanum ( $C_{La} + C_e$ ) determined based on spectrographic analyzes, can be up to 0.2% (Popuiac, 2013).

## V. Discussions and conclusions

Several researchers consider that the metamorphic rocks of gneisses formation are derived from basic volcanic protoliths, montmorillonite and vermiculite clays genetically related to the mafic volcanics and some subordinate quantities of polymictic and grauwacke sandstones. On the basis of the existing theoretical concepts it is assumed that the paragenetic association commonly found in the gneisses formation was generated at temperatures of about 600-750° C under the conditions of overburden pressure of about 4 to 8.5 kbar (Zaharov et al., 1987). At the same time, the rocks in the gneisses formation can be seen as *raw material* for the rocks generated by later ultrametamorphic processes. Probably, because of their refractory behavior, the accessory minerals were inherited without significant changes from their source rocks. This is supported by the geochronological research data conducted by Ukrainian geologists. In the south-west slope regions of Ukrainian Crystalline Shield - neighboring area of Dniester river basin - zircon age found in the Archean, early Proterozoic and late Proterozoic formations is practically one and the same, of about 3000 million years.

It is not excluded that metasomatic processes in the Dniester basin region, according to regional tectonic evolution, were produced repeatedly.

Being established in the early Archean, the portion of the crust studied here ended its tectonic evolution approximately at the beginning of the early Proterozoic. Probably, during that period, in this zone, magmatic processes were accompanied by horizontal and vertical movements of the basement, which led to the formation of the Dniester graben, poorly outlined because of a series of transverse faults. The tectonic features of the basement have influenced the sedimentogenesis processes that took place in the Riphean and early Vendian, and the basal layers, consisting of terrigenous lithological varieties, are almost entirely correlated with the petrographic composition of the basement, reflecting the mineralogy of the the most elevated paleomorphologic structure of the basement. This explains the relatively great thickness of sedimentary layers along the Dniester fault and, most important, the generation, in some places, of detrital aureoles rich in monazite and zircon, which are reflected geochemically by REE geochemical anomalies, especially rich in Lanthanum and Cerium.

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## THE METALLIC CONTAMINATION IMPACT ON FRESHWATER MUSSELS *ANODONTES* AT THE SAINT-VICTOR-SUR-LOIRE LAKE, FRANCE

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**Abstract:** Saint Etienne (France) has a large industrial and mining history. The end of these activities has given way to industrial wasteland and mine dumps. Leaching caused by rain, industrial and mining waste may generate a very large urban pollution. Rivers (Ondaine and Loire) and lakes (Saint-Victor-sur-Loire) downstream of this zone are highly polluted by heavy metals. The study has focused freshwater mussels to determine the risk of water pollution. We have shown that freshwater mussels are a good bioindicator for monitoring over time, this type of water pollution due to their ability to filter water from the river. The entire food chain (freshwater mussels, mollusk, shrimp, fish, birds and humans) is affected by the pollution.

**Keywords:** freshwater mussels; heavy metals; bioaccumulation; bioindicator.

### 1. INTRODUCTION

Due to their industrial and mining history, several agglomerations in the Rhône-Alpes region have mining and industrial wastes containing several metals pollution sources of groundwater, public health and urban management problem of some sites.

The study of pollution of the Saint-Victor-sur-Loire Lake lacks. Indeed, considering the difficulty of the collection of valid samples for trace metal analysis in water as well as the low spatial and temporal representativeness of these, the use of the quantitative bioindicators of the chemical contamination attracts more and more attention in ecotoxicology.

We have elaborated this work to estimate the degree of the metal contamination at the level of the Saint-Victor-sur-Loire Lake and Ondaine river mouth this by dosage of seven trace metals (Cu, Mn, Fe, Co, Cr, Pb and Cd) in freshwater *Anodonta* mussels. In fact, freshwater mussels have been found to be suitable indicator species for trace metals (Goldberg, 1975; Phillips, 1976; Phillips, 1977; Brown & Luoma, 1995; Jumshamn & Grahl-Nielsen, 1996). It is capable to accumulate trace metals such as cadmium, mercury and lead to a larger extent than for example fish and algae (Jumshamn & Grahl-Nielsen, 1996; Riget et al., 1996; Airas et al., 2004).

### 2. CONTEXT

Saint Victor Lake is bordered by two castles; it is a reservoir of 66 million m<sup>3</sup> of volume, 3.65 km<sup>2</sup> surface, built in 1957. Decennial drains in 1977, 1987 and 2000 were not performed. They were conducted between 2011 and 2012. Saint Victor Lake is located downstream of Aurec-sur-Loire (Haute-Loire) and upstream of Saint-Just-Saint-Rambert (Loire). The density of carp is low but includes catfish, crayfish and mussels. In March 1995, the volume of sludge deposited at Ondaine mouth was estimated at 40 000 m<sup>3</sup>. The cost of sludge removal was evaluated then at € 2 million. The total volume of sludge deposited across the Grangent dam was between 1.5 and 2 million m<sup>3</sup>, which represents 1.3 Mt. Two-thirds of the sediment would have been deposited by the Loire River and a third by tributaries (primarily Ondaine). Among the sediments, there were found metal oxides in significant quantities. The thickness of the sediment was about 5 meters at the confluence of Ondaine-Loire. Water quality is still a major problem for the Saint Victor Lake. Indeed, during the heart of the great industrial period, Ondaine brought 20,000 tonnes of materials such as iron, manganese, zinc and nickel.

Ondaine is an affluent of the Loire River, crossing several small towns. The Ondaine River itself has several tributaries: The Cotatay has long time been renowned for the quality of its waters. Twenty-two ancient factories located on its shores, ended their industrial activity. The Egotay's Ondaine tributary was also renowned for the quality of its waters. Many laundresses and Unieux washerwomen were

washing their line basins using its waters. Since the late 1960, the quality of rivers has deteriorated. In November 2002, the Egotay was still receiving Charles's area wastewater and the ones of Beaulieu town, located in the town of Roche-la-Molière, and domestic discharges of Bécizieux, the small town of Saint-Victor-sur-Loire via a collector of sewage and other agricultural and industrial untreated waste. The first traces of pollution of the Gampille tributary of the Ondaine were identified in 1964. In 1989, the Agency of Loire-Brittany Basin is committed to the Department of the Haute-Loire to stop the pollution problems of the Gampille and its tributary Combobert, caused by the waste disposal of Saint-Just-Malmont and the malfunction of the treatment plant.

The causes of "historic" pollution of the Ondaine river have many origins: Industrialization of the valley, receives, without any treatment, waste waters from many industrial plants; tailing mine and industrial waste; direct discharges of wastewater into the river; the small size of the watershed that provides the preponderance of urban discharges during low flow periods and the excessive and uncontrolled use of pesticides also contributes to the degradation of Ondaine and Loire water quality.

The mines are no longer operating in the Ondaine Valley since 1983. The basement of the valley contains 304 galleries. Mine wastewater was pumped by the Charbonnages de France Company but rejected in part on the bed of the Ondaine watercourse. The slag wastes are still important. The management of these historical slag wastes still constitutes to be a major problem for the region. For 150 years, many companies operated production of special steels but dairy has accumulated in many slag wastes. The sources of pollution of the river were still potentially important in 2003. Industrial equipment is not completely waterproof. Wastes were sometimes stored near watercourses. A preliminary study by Geosciences & Environment department of Ecole Nationale Supérieur des Mines de Saint Etienne of a one hundred samples showed that the soils of the Ondaine valley are very rich in metal oxides, especially those growing on industrial waste. Industrial waste and harvested soils are highly reactive (Figure 1) and metal oxides are mobilized and easily pass into solution. Water filled metal oxides exceed safety standards. Leaching tests conducted in the laboratory have shown that water charged resided 3-4 days, depending on the location, before returning to the streams and Ondaine River.

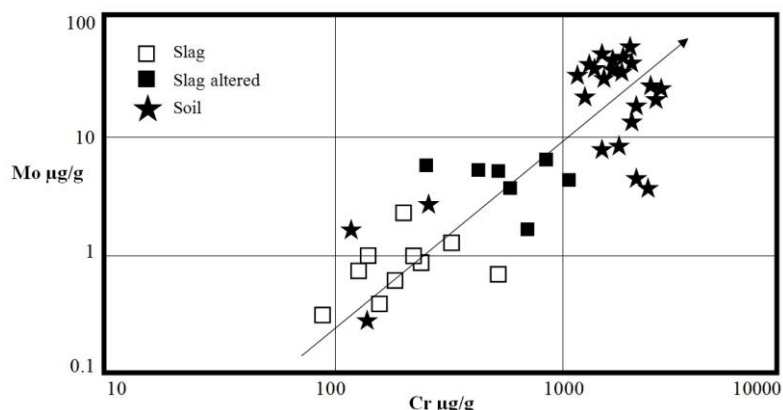


Figure 1: Mo versus Cr content from slag, altered slag and soil of Ondaine valley.

## 2. METHODS AND MATERIALS

The sampling of freshwater mussels was elaborated at four stations belonging to the mouth of the Ondaine estuary and Saint Victor Lake.

The shells were carefully opened so as not to damage the tissues. The samples were conserved in sterilized petri dishes, weighed and stored at a temperature of -18 °C. The adopted procedure for the preparation of mussels was as follows: lyophilization during 48 hours under vacuum and a temperature of -50 °C, and under a pressure of about 4000 bar; grinding of each sample in a porcelain mortar until the obtaining of a fine powder; Addition of 3 ml of concentrated HNO<sub>3</sub> (69°C) in each bomb to solubilize the metals and 1 ml of H<sub>2</sub>O<sub>2</sub> to oxidize the organic matter and digestion at high pressure and high temperature. Analyses of the final solutions were done for all trace elements detected by ICP-AES and Atomic Absorption Spectroscopy in graphite furnace. The results are expressed in µg/g of dry weight (ppm).

Scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS). Observations and elemental analyzes were performed on a scanning electron microscope Jeol JSM 6400 coupled to an Oxford EDS analyzer (ENSM-SE). Observations were carried out on secondary electrons mode in the case of granular raw unpolished samples and backscattered electron mode. To obtain

comparable results, all analyzes were performed under identical conditions with an accelerating voltage of 20 kV. Chemical analyzes are semi-quantitative. Mappings XR heavy metals helped to highlight their distributions in mussel shells. Previously, samples were metallized with carbon or gold depending on the type of observations and analyzes made.

### 3. RESULTS AND DISCUSSION

The organic portion of these freshwater mussels is richer in metals than the shell (Figure 2). The freshwater mussels filter the water of the river and therefore concentrate metals in the organic part. Metal concentrations are above the safety and health standards (Bilal, 2013). Ondaine Valley drains the major part of the heavy metals that we find in freshwater mussels. The contents of heavy metals in both cases, Loire River and at the mouth of Ondaine, are comparable. The same pattern is found in the freshwater mussels of the Ribeira de Iguape River in Brazil and the freshwater mussels from Sebu River in Morocco. The processes of accumulation in tissues are extremely complex and depend on several factors, including the properties of the receiving tissue (Maury & Engrand, 1986); the nature of the contaminant and the intra and extracellular environment (Bowen, 1966). Contrary to fishes, the organs of the freshwater mussels are all exposed to chemical pollutants suspended in the water; direct contamination could have the same significance as the trophic contamination.

Heavy metals are in relationship with different pollution incidents and continuous leaching of industrial and mining waste. Mo, V and Co get to permanently control the composition of mussel's shells. Fe, Mn, Ni appear sporadically (Figure 3) and indicate an occasional pollution. The striations of these shells show growth and it represents a very good bioindicator to monitor the pollution of water.

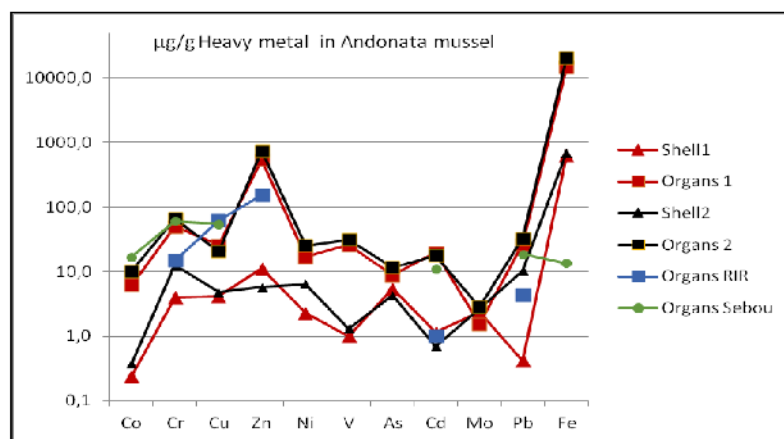


Figure 2: Distribution of metals in freshwater *Andonata* mussels at the Saint Victor Lake, Loire river (Shell1, organs 1), at the mouth of Ondaine, Shell 2 and organs 2 (Bilal, 2013) and freshwater mussels at the Ribeira de Iguape River, organs RIR, Brazil (Rodrigues et al., 2013) and green: Organs from Sebou River Morocco (Bounakhla et al., 2011) .

### 4. CONCLUSION

Understanding the phenomenon of bioaccumulation of heavy metals in living substance is of extremely complex. This is due to the interpenetration of several parameters which influence the bioaccumulation namely in general: the physico-chemical characteristics of the environment, the chemical properties of the contaminant and the biologic factors of the organism. The freshwater mussels are reliable as bioindicator and easy to use to track the evolution of water pollution.

This study showed that all measured heavy metals are higher than normally permitted levels and reveal a health hazard for the population. Notably, Saint-Victor-sur-Loire Lake is a station where take place a lot of nautical activities and swimming from spring to late summer.

In conclusion, the results of this study show the persistent degradation of the Ondaine Valley and Loire River as a result of industrial, mining, agricultural and domestic discharges, which it would increase if no strategy of protection of this environment by concerned authorities, is developed and implemented.

### 5. ACKNOWLEDGMENTS

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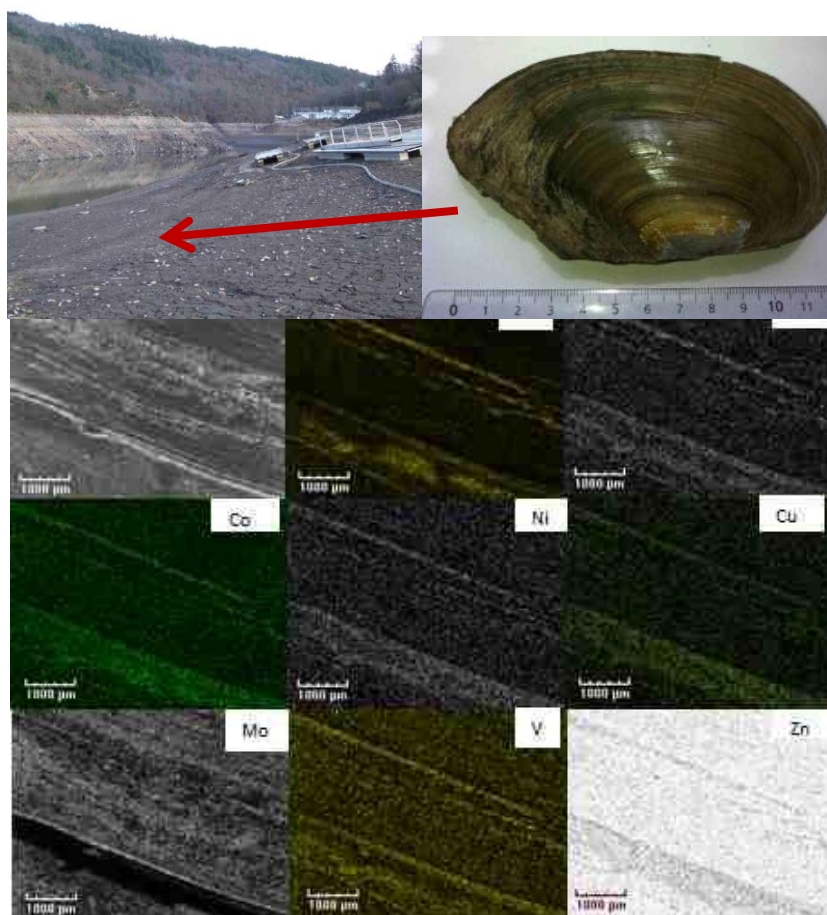


Figure 3: SEM image and heavy metals distribution in the shells of freshwater mussels by XR mapping (Bilal, 2013). Fe, V - yellow, Mn, Mo, Ni - white; Co, Cu - green and Zn - grey.

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## SURFACE MINING OF THE ROMANIAN MINERAL AND POWER RESOURCES, IN ALL TIMES

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**Abstract:** During his entire history, in Romania, 82 mineral and power substances were exploited at the surface, in over 3478 identified quarries and open pits. Exploitation period began timidly in the Primitive Commune. In Antiquity, it was done at a moderate rate in the Dacian Kingdom period and at high level in the Roman Empire time. Surface mining have regressed in first part of the Middle Ages (the migration period) but, in the second part, the mineral resources exploitation grew. However, the biggest intensity of surface mining and mineral production, the most numerous mineral resources (81), quarries and open pits (3,383) are observed in Modern Ages. In all times, 98,6 % (3427 quarries and open pits) from the identified surface exploitations had extracted 78 non-power mineral resources and 1,4 % (51) had exploited 4 power resources. There were 3,301 non-metallic surface exploitations and only 6 metallic mineral resources were exploited in 126 quarries. The non-renewable resources type (79 substances) were extracted in very large quarries and open pits number: 2,390 (68.8 %).

**Keywords:** surface mining, Romanian surface mining, mineral resources exploitation, Romanian quarries, Romanian open pits.

### INTRODUCTION

Mineral and power resources are of fundamental importance for economic development of all countries. Although Romania is not a big country, due to the very complex geological structure 110 mineral and power substances have been identified and quantified as resources and reserves (Marinescu, 2003). In time, the most numerous (82) from these substances were exploited at the ground surface (the statistics go back to the year 2000).

Currently, Romania ranks 10<sup>th</sup> in the world in terms of the diversity of minerals produced in the country. Around 60 different mineral commodities are produced in Romania (Taylor and Francis, 2007, from Wikipedia). The surface mining is a very old occupation for our people and its real size is not properly known. In time, this presentation must to be continuously improved, especially with new archaeological data and old documents studies.

### 1. FAVOURABLE FACTORS FOR THE SURFACE MINING

Located between the latitude coordinates of 43°37'07" and 48°15'06" North and longitude coordinates of 20°15'44" and 29°41'24" East, Romania is an intersection point for commercial roads, from North to South of the Europe and From East to West (Eurasian Steppe Route from Silk Road) but also to numerous neighboring peoples. The country extends approximately 300 miles North to South and 400 miles East to West and have a surface of 237,500 km<sup>2</sup>. In time, the population was numerous, with a good density, laborious, stable. On this territory, very old civilizations existed.

New archaeological discoveries on the Sibiu –Orăștie highway show 8,000 – 10,000 years old habitation. The Tartaria tablets indicate the oldest writing in the world (7,300 years old). The Cucuteni Civilization is 7,000 years old (some hundred years before the first localities in Sumer and Egypt), Boian Civilization is 6,500 years old, Gumelnița Civilization is 6,000 years old, Hamangia Civilization is 5,500 – 6,000 years old. On the Romanian Territory, there was a non-intermittent civilization (population continuity on 5,000 years to present).

The economic development was uninterrupted in time but with increase and decrease periods. The relief variety (mounts, hills, plains and plateaus) and dense hydrographical network had permitted quarries, respectively sand pit, gravel pit or ballast pit existence. The geological structure was mainly determined by:

- many and different geo-structural units: Eastern Carpathians, Southern Carpathians, Apuseni Mountains, Moldavian Platform, South-Dobrogean Platform, Central Dobrogean Massif, North-Dobrogean Orogen, Transylvanian Depression, Pannonian Depression etc.
- long geological evolution in time, with many orogen cycles: pre-Assyntic, Assyntic, (Cadomian), Caledonian, Hercynian (Variscan), Alpine;

- presence of 110 mineral and power substances, identified and quantified in resources and reserves; the most numerous (82) of these were at the surface and at small depth.

## **2. SURFACES MINING ON HISTORIC EPOCHS**

### **2.1. SURFACE MINING IN THE PRIMITIVE COMMUNE**

Of course, the surface mining was practiced in primitive manner. Archaeological data indicate as certain only 4 exploited mineral substances: firestone (extensively exploited but the archaeologists discovered exploitations only at Bercea Mare, Leșnic and Roșcani), quartzite (Cernat Hill), limestone (Gura Văii), sand and gravel (Ghioroc).

Surface mining was practiced in other numerous, but unknown today sites, especially firestone and quartzite, on Dârjovului Valley, Oltului Valley, Dâmbovniciului Valley, Lupului Valley, Prutulului Valley (Marinescu, 2013).

### **2.2.SURFACE MINING IN THE ANTIQUITY**

In the Dacian Kingdom period andesite quarries existed at Uroi Hill (Simeria town) and Pietroasa Hill (Deva city). Limestone quarries are known at Măgura Hill (on Streiului Valley), Călan and Ardeu. Sand was exploited in Ghenetea open pit. Gold was extracted from gold sands (in many unknown river exploitations) (Marinescu and Bogatu, 2005). Using andesite from Pietroasa Hill, the well known sanctuaries from the Sarmizegetusa Regia have been constructed.

The archaeologists (Boroneant, 2000) speak about indeterminate rocks exploitations at Bejan Hill (near Deva city), Dugău Hill (Ionești), Făget and Grădiștea (Sf. Maria de Piatră) quarries. We think many of the remains of the Dacian quarries have disappeared because the exploitation have continued, with increased intensity, in Roman times.

In Roman Empire period, the number of identified quarries and open pits is 53. Limestone quarries were identified at Măgura Hill (Călan), Cărpiniș, Geoagiu, Peșteana, Strei (Călan), Valea Sângiorgiului (Călan), Ampoița, Ighiu, Albești, Iablanița, Rușchița, Rusca Montană, Bahna, Gura Văii I, Gura Văii II, Vâciorova and Dinogetia (Garvan). Large quantities of marble were extracted at Pârâului Valley (Cristur), Rușchița and Rusca Montană (possible, Bucova as well). Andesite quarries are known at Petris-Uroi (Simeria city), Pietroasa Hill and Pietroasa 2 (both near Deva city).

The andesite from Petris-Uroi was used for buildings from Ulpia Traiana Sarmizegetusa, Micia and other roman localities (Boroneant, 2000). Sandstone was exploited in quarries at Petnic, Rusca Montană, Verendin; dacite at Creaca Tîclar and travertine at Breznița and Geoagiu. Sand and gravel were probably extracted in many places but only Ghioroc open pit is known.

Surface mining of the iron was done at Teliucu Inferior and other unknown exploitations. Gold surface mining was very intense. It was extracted in Roșia Montană, Măgura Tebei, Vulcoi – Corabia, Boteș quarries or from alluvia, in non-identified places on the rivers Aries, Mureș, Crișul Alb, Jiu, Olt, Caraș, Nera. From this period, the archaeologists indicated many indeterminate rocks quarries: Deva, Sfântă Măria de Piatră 1 and 2 (Călan), Cârjiți 1 and 2, Banița, Bejan, Săcel, Sfântă Măria Orlea, Strei, Streisângiorgiu, Valea Sângeorgiului (Călan), Dealul Dugău (Ionești), Cernavodă Pod, Baci, Urișor, Podeni, Săndulești (Turda), Vodița.

### **2.3.SURFACE MINING IN THE MIDDLE AGES**

In the first part of Middle Ages (migration period) there was not a strong state in any of the Romanian provinces and identified surface mines are very few. However, in the second part, the exploitation intensity increased and the identified quarries and open pits are about 25.

In this period were exploited: limestone (Ardeu, Rușchița, Rusca Montană, Malu Roșu, Jucu de Sus, Podeni, Săndulești Nord, Gura Văii, Ogradena Veche, Dinogetia), chalk (Murfatlar), marble (Rușchița and Rusca Montană), sandstone (Luncavița, Mehadica, Rusca Montană and Verendin, calcareous tuff (Topleț, Ilisova, Maceris, Svinița, Pescari), argillaceous schist (Băile Herculane), iron ore (Teliucu Inferior) (Marinescu, 2013).

### **2.4. SURFACE MINING IN THE MODERN AGES**

In the presented historic epochs, the number of identified quarries and open pits do not exceed 95 (and the number of mineral substances have exceeded 15) but in reality, logically, there must have been several

thousands which we do not know about. In Modern Age (the research goes back to the year 2000) 3,383 quarries and open pits, identified up to now, have extracted approximately 82 of mineral substances.

Due to the biggest economic development in the 1947-1989 period there were registered the most numerous quarries and open pits. If it is to compare 95 locations with 3,383 surface mines, the conclusion is evident: all surface mining statistic is approximated by the modern age statistics!

### 3. SURFACE MINING ON RESOURCES GRUPES

Only 4 power substances were exploited at the surface of the ground, in 51 quarries: lignite (45 quarries), pit coal (3), bituminous schist (2) and bituminous sand (1). Most substances (78) were non-power and for their extraction was used a very large number of identified open pits and quarries: 3,427 (Marinescu, 2013). 6 metallic mineral substances, misnamed metallic ores, were exploited: ferrous ores (9 quarries), manganese ores (4), copper ores (4), bauxite (101), gold-silver ores (6), complex (lead, zinc, copper) ores (2). The total number of metallic ores quarries was 126. The most exploited substances (77) were non-metallic and for their extraction have been used a very large number of identified surface exploitations: 3,378 (Marinescu, 2013). In 1088 open pits were extracted 4 mineral substances, supposed renewable: sand (172 open pits), gravel (127), sand and gravel (789) and ballast (sand + gravel + boulder; 8). The exploited non-renewable type (79 substances) was extracted in very large number: 2,390 (68.8 %) quarries and open pits.

### 4. SURFACE MINING ON COUNTIES

Due to the different geological conditions and economic development, the surface mining in 41 actual counties (in time, Romania lost many counties from his territory) and the Bucharest capital is very unequal. In each county, the number of the quarries and open pits (the substances number in parenthesis) are the following: 294 (38) Hunedoara, 220 (19) Bihor, 216 (25) Tulcea, 180 (15) Constanța, 173 (27) Cluj, 162 (21) Maramureș, 148 (27) Arad, 133 (14) Suceava, 132 (14) Covasna, 124 (16) Brașov, 113 (29) Caras Severin, 105 (19) Harghita, 101 (10) Gorj, 96 (18) Sălaj, 94 (19) Alba, 85 (12) Prahova, 84 (6) Iași, 81 (22) Mehedinți, 78 (11) Argeș, 78 (7) Buzău, 74 (8) Dâmbovița, 73 (14) Satu Mare, 67 (13) Sibiu, 57 (10) Bistrița-Năsăud, 56 (13) Vâlcea, 55 (6) Bacău, 52 (11) Timiș, 50 (5) Vrancea, 44 (7) Mureș, 39 (8) Botoșani, 34 (1) Giurgiu, 30 (6) Neamț, 26 (4) Dolj, 25 (3) Olt, 17 (3) Galați, 16 (4) Ilfov, 16 (3) Teleorman, 14 (3) Ialomița, 14 (6) Vaslui, 11 (2) Călărași, 8 (4) București, 4 (2) Brăila.

### 5. SURFACE MINING ON MINERAL AND POWER SUBSTANCES

There is a big discrepancy between surface mining on mineral substances groups, generally, and on mineral and power substances, especially. 3086 quarries and open pits have exploited rocks, 215 industrial minerals, 126 metallic minerals and only 51 power resources (Fig.1).

From all substances, the first five (sand and gravel, limestone, common clay, andesite, sandstone) were exploited in 2072 quarries and open pits and the remaining 77 substances in only 1406 (Fig.2).

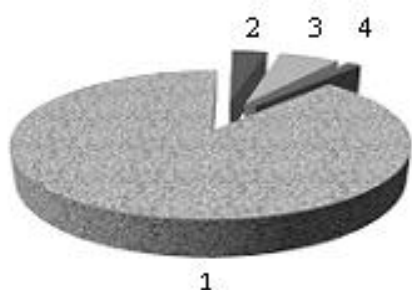


Fig. 1. Surface exploitations percents on rocks (1), metallic ores (2), industrial minerals (3) and power substances (4) groups.

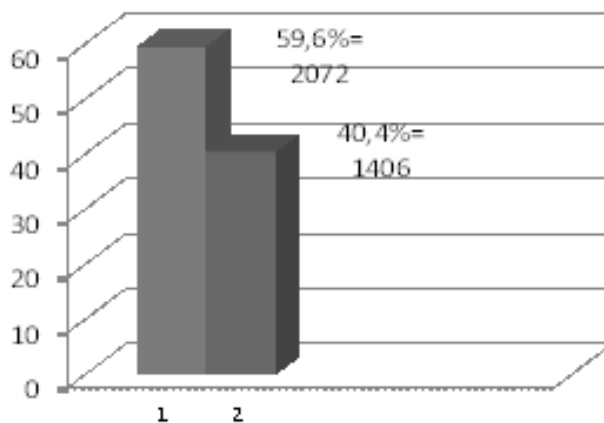


Fig. 2. Surface exploitations percents on the first five exploited substances (1) and the other 77 substances (2).

## 5.1. SURFACE MINING OF THE ROCKS

### 5.1.1. Sedimentary rocks exploitations

Surface mining of sedimentary rocks (76 %) was the most important among all rocks (see Fig.3). With 789 quarries and open pits, sand and gravel were not only the most exploited sedimentary rocks but also the most exploited mineral substances. Practically, they were extracted in open pits. The most important rivers where sand and gravel open pits existed are: Someș, Tur, Crasna, Iza Mara, Lăpuș, Vișeu, Bistrița, Suceava, Siret, Jijia, Prut, Someșul Mare, Someșul Mic, Arieș, Mureș, Târnava, Olt, Crișu Negru, Crișu Pietros, Crișul Repede, Mureș, Strei, Dunăre, Cerna, Nera, Moldova, Trotuș, Ozana, Milcov, Topolnița, Gilort, Motru, Sohodol, Amaradia, Topolog, Vâlșan, Argeș, Raul Doamnei, Ialomița, Cricovul Dulce, Prahova, Teleajen, Dâmbovnic, Ciorogârla, Buzău, Râmnicul Sărat, Siret and Ialomița rivers. The limestone (common and ornamental) was the second exploited mineral substance. It was extracted in many counties and the number of quarries is very large, too: 599. Out of these, 14 have extracted ornamental limestone. The quarries are distributed only in the mountain, hill and plateau area of the counties.

Five kinds of clays were exploited in all times, but the common clay (252 quarries in 38 counties and Bucharest) was the most important. Remaining types of clays will be discussed at industrial minerals. 214 surface mining of the sandstone were registered in 31 counties, with two varieties: common (213 quarries) and ornamental (1). 172 open pits and quarries in 33 counties and Bucharest, have exploited sand. Approximately 2/3 of sand surface exploitation were open pits and they have been worked along the rivers in 31 counties and Bucharest. The remaining 60 sand surface exploitations were quarries. From all gravel surface exploitations, in 25 counties, 109 were open pits and 18 quarries.

More dolomite-limestone and less dolomite, were extracted in 46 identified quarries, from 11 counties. Other sedimentary rocks exploitations were on: sandstone and conglomerate (32 quarries), marl (24), conglomerate (17), chalk (12), loess and loessoid clay (15), travertine (21), diatomite (11), calcareous tuff (8), marl-limestone (1), clay-schist (1).

### 5.1.2. Magmatic rocks exploitations

In all times, surface exploitations of these rocks represented 17,8 % from all surface mining of the rocks (Fig.3). The andesite is the most exploited magmatic rock. It was extracted in 133 of identified quarries from 14 counties, located in the Apuseni Mountains, Eastern Carpathians (Oaș, Gutâi, Țibleș, Rodna, Bârgău, Călimani, Gurghiu, Harghita Mountains) and in South Carpathians. Supplementary, some (identified 3) surface mining for ornamental andesite existed.

After exploitation intensity, at big distance from andesite dacite tuff follows, extracted in ten counties. It is the most exploited tuff (60 quarries) comparatively with other tuffs: andesite tuff (5) and basalt tuff (4). Apuseni Mountains, South Carpathians and North-Dobrogean Structogen are known with many granite resources. Common granite quarries were registered in 8 counties with 50 identified surface exploitations. The ornamental granite quarries, were identified only in Tulcea county, at Dealul Șerparu and Greci.

At small distance are situated the dacite (47 quarries from 6 counties) and basalt (41 from 10). The dacite was described for the first time as a volcanic rock type in Romania, at Poieni, which is the "locus typicus". Supplementary, the old varieties of basalt, named diabase, were extracted in 10 quarries from 5 of the counties. The granodiorite resources are located in Apuseni Mountains, Southern Carpathian and North-Dobrogean Structogen. Common granodiorite was exploited in 21 quarries from 7 counties. The rock extracted at the Piatra Îmbulzita quarry, near Greci locality (Tulcea counties), was used as ornamental stone.

The rhyolite resources exist in the following geostructural units: Apuseni Mountains (Vlădeasa Masiff), Eastern Carpathians and North-Dobrogean Structogen. It was extracted in 20 identified quarries, in 5 counties, especially in Tulcea county. It is known that the diorite resources were located in Apuseni Mountains (Zarand, Banatului, Meseș, Poiana Ruscă, Bihor Mountains), Southern Carpathians (Vulcan Mountains) Northern Carpathians (Oaș Mountains), and North-Dobrogean Structogen geostructural units (Marinescu, 2013). 18 quarries in 6 counties extracted diorite. Other magmatic rocks surface exploitations were: perlite (11 quarries), andesitic agglomerate (4), gabbro (3), basaltic scoria (2), sienite (2), dolerite (2), peridotite (1), trachite (1).

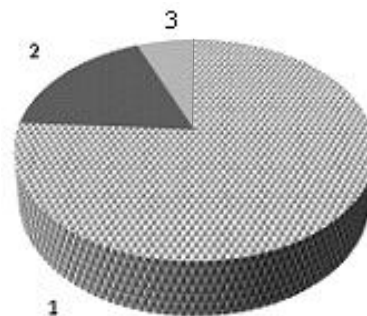


Fig. 3. Rocks surface exploitations percents on sedimentary (1), magmatic (2) and metamorphic (3).

### 5.1.3. Metamorphic rocks exploitations

Marble and crystalline limestone resources exist in metamorphic formations of the Apuseni Mountains, Eastern Carpathians (Lăpuș, Maramureș, Bistriței, Rodna, Gurghiu Mountains), South Carpathians (Făgăraș, Poiana Ruscă, Lotrului, Căpățânei, Almăj and Cindrel Mountains) and North Dobrogea Plateau (Tulcea Hill). They were continuously exploited, from old times. Their surface mining is known in 17 counties (98 quarries). Quartzite resources exist in many areas with crystalline formations of the Eastern Carpathians, Southern Carpathians, Apuseni Mountains and in the Triassic or Devonian formations from North-Dobrogean Structogen. They were extracted in 24 quarries from 7 counties, especially in Tulcea county.

The greenschists are specific for the Central Dobrogean Massif geosstructural unit. Accordingly, they were extracted in 23 surface exploitation, only in the two counties from this unit: Tulcea and Constanța. The gneiss resources are widespread in areas with crystalline formations, especially in Southern Carpathians geosstructural unit (Făgăraș, Cozia, Cibin, Sebeș, Lotru Mountains etc.).

Here they were exploited in 17 quarries from 7 counties. Other metamorphic rocks surface exploitation were: mica-schist (12 quarries), serpentine (12) and amphibolite (10).

### 5.2. SURFACE MINING OF THE METALLIC ORE RESOURCES

Surface mining for metallic ores resources was done for iron ore, gold-silver ore, copper ore, bauxite, complex ore and manganese ore. In time, iron ore (siderite) was extracted in many unidentified old quarries from Poiana Ruscă Mountains (Hunedoara county) but known quarries are only Teliuc I-V, Teliucu inferior, Ghelari and Vadu Dobrei. At Căpuș deposits (Cluj county), oolite iron ore was extracted in some perimeters but the number of quarries is unknown.

Gold-silver ore quarries existed in Alba (Măgura Țebei, Boteș), Hunedoara (Certej, Roșia Montană, Vulcoi-Corabia) and Maramureș (Șuitor and possible Baia Sprie) counties. Copper ore was extracted in Alba (Roșia Poieni quarry), Caraș Severin (Moldova Nouă) and Hunedoara (Deva, Valea Morii) counties. The bauxite data are not very sure about the quarries number. These existed and were exploited only in Bihor and Hunedoara counties, in approximately 100 quarries. Surface mining for complex ore existed only in Hunedoara county (Coranda-Hondol, Valea Morii quarries) and manganese ore only in Suceava county, in small quarries (Arșita, Căprăria, Dadu, Oița).

### 5.3. SURFACE MINING OF THE INDUSTRIAL MINERALS RESOURCES

22 industrial minerals resources were exploited in 204 quarries. After all data, gypsum resources were identified in the Transylvanian Basin, South Carpathians, Eastern Carpathians and in Moldavian Platform. It was extracted in 44 quarries from 9 counties. Very important were the infusible clay, exploited with 39 quarries from 11 counties. Surface mining for bentonite and bentonite tuff was done in 26 quarries from 8 counties. Colored earths are clays with iron and manganese oxides in their composition. They were extracted in 14 quarries from 8 counties.

Other industrial minerals surface exploitations were: kaolin clay (13 quarries in 4 counties), kaolin sand (4; 1), perlite (11; 1), common kaolin (8; 4), pegmatite feldspar (8; 3), baryte (6; 2), pegmatite mica (6; 3), quartz (4; 4), talc (4; 2), kaolin sand (4; 1), aragonite (2; 2), graphite (2; 1), alabaster (2; 1). At small scale (single quarry) were extracted: calcite (Valea Ponor quarry), sulphur (Negoiul Românesc), celestite (Copăceni), magnesite (Tișovița) and asbestos (Eibenthal).

### 5.4. SURFACE MINING OF THE POWER RESOURCES

The lignite quarries (Marinescu, 2013) were and are located in Argeș (Pescăreasa), Bihor (Voievozi), Covasna (Vârghiș, Racoș, Sfântu Gheorghe), Gorj (Tismana I-II, Peșteana Sud, Jilț Nord, Jilț Sud, Vulcan, Moi, Pinoasa, Runcurel, Mătășari, Meris 2, Balta Unchiașului, Căceni, Gârla, Beterega I-II, Poiana, Lupoia, Peșteana Nord, Roșia de Jiu, Horezu, Aninoasa, Bustuchin, Fărcașești, Ploștina Nord, Ploștina Sud, Rovinari Est, Roșița, Ruget, Tehomir, Timișeni-Pinoasa, Valea cu Apă, Urdari), Mehedinți (Husnicioara, Husnicioara Est, Husnicioara Vest), Prahova (Malu Roșu, Filipești), Vâlcea (Alunu, Berbești, Olteț) counties. Pit coal was extracted in Hunedoara (Uricani, Câmpul lui Neag I-II quarries), bituminous schist in Caraș Severin (Anina, Doman) and bituminous sand in Prahova (Măța) counties. Some brown coal quarries have existed but they are unknown.

## 6. ACTUAL SURFACE MINING

In February 2014, the National Agency for Mineral Resources (NAMR) published on the internet the exploit permits and licences for all mineral and power substances. In 2014, pursuant to these documents, private and state companies will exploit 52 mineral substances (andesite, ornamental andesite, alabaster, anhydrite, amphibolites, basalt, bentonite, calcite, kaolin clay, kaolin sand, common clay, copper ore, dacite, diabase, diatomite, diorite, dolomite, gypsum, gold-silver ore, granite, granodiorite, green schist, limestone, limestone with brucite, ornamental limestone, loess, marble, marl, marl-limestone, mica-schist, pegmatite with feldspar, perlite, quartz, refractory clay, rhyolite, sand, sand and gravel, siliceous sand, serpentine, slate, therapeutic mud, travertine, tuff) and power substances (brown coal, lignite, peat) in 1252 quarries and open pits from 39 counties (internet data, after NAMR). It will also be exploited the mining waste.

From these permits and licences, 892 represent exploit permits for 29 mineral and power substances (686 for sand and gravel) and 360 exploit licenses for 48 mineral and power substances (87 for sand and gravel).

## CONCLUSIONS

Due to the very complex and favourable geological structure, Romania has 110 mineral and power substances identified and quantified in resources and reserves. In time, from the Primitive Commune to present, the most numerous (82) from these substances were exploited at the ground surface, in over 3,478 of identified quarries and open pits. Of course, the real number of surface mines is bigger and unknown, especially for the old times.

According to the existent permits and licenses, in 2014, private and state companies will exploit 52 mineral and power resources, in 1252 quarries and open pits from 39 counties.

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## GEOLOGICAL SOURCES FOR ARCHAEOLOGICAL OBSIDIAN FOUND IN ROMANIA

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**Abstract:** Obsidian is widely considered an ideal material for geological source tracing using elemental methods of analysis. To identify the sources for obsidian prehistoric tools in Transylvania, Banat and Southern Muntenia, XRF (X-Ray Fluorescence) and milli-PIXE (Proton Induced X-ray Emission) methods were used to detect Rb, Sr, Y, Zr, Ti, Mn, because their values strongly differ from one source to another. The majority of Transylvanian Neolithic samples fit the Carpathian II pattern (Hungarian Tokaj Mountains). The Carpathian I pattern (Slovakian Tokaj Mountains) can be attributed to the Neolithisation period samples both for Cuina Turcului (Southern Banat – Iron Gates) and Măgura (Southern Muntenia – Teleorman County). For Cuina Turcului Mesolithic samples the situation is special, they could fit Carpathian II pattern but two of them are close to Melos values, so, more samples from this category must be analyzed and an archaeological discussion is necessary.

**Keywords:** Obsidian geological sources, Neolithic tools, X-Ray Fluorescence, milli-PIXE.

### Introduction

Obsidian is a natural volcanic glass (<http://www.mindat.org/min-8519.html>), widely used for prehistoric stone tools and traded over long distances. In Romania, obsidian archaeological items were found in Transylvania, Banat - near Danube border with Serbia, and Southern Muntenia. Their geological sources are supposed (Biró and Dobosi, 1991) to be Tokaj Mountains (now in Hungary and Slovakia), Greek Aegean Islands, Lipari Island, Armenia or Anatolia where are situated the closest obsidian deposits (Fig. 1).



Fig. 1. Geographical locations of archaeological sites and geological obsidian sources.

Obsidian is known from several volcanic regions in Europe, some of them still active as obsidian mining. **Greek islands** - situated in the Aegean Sea, the most famous source of obsidian is Melos, lying closest to the mainland.

**Asia Minor** - Western and Central Anatolia. Several obsidian sources spread on the Anatolian peninsula; in the Caucasus, literally mountains of high quality volcanic glass crop out, serving as raw material for Armenian settlements since the Lower Palaeolithic.

**Italy** – obsidian was formed during several periods of the Pleistocene due to active volcanism in the Tyrrhenian Sea (Sardinia, Palmarola, Lipari).

**Carpathian basin** - three occurrences of obsidian are known along the north-western side of Neogene volcanic chain from Eastern Carpathians which are now spread on the territory of three countries (Slovakia, Hungary, and Ukraine), as follows:

**Slovakia (Carpathian I):** the source of obsidian is situated on the eastern margin of the Tokaj hill built up of the so-called Zemplén rhyodacite of 15-16 Ma (Dobosi, 2011). Obsidian from this source is of very good quality for stone tools. Obsidian occurs as nodules embedded in rhyolite tuffs.

**Hungary (Carpathian II):** in the southern part of the Tokaj-Presov Mts. there are two obsidian sources related to 9-10 Ma volcanic eruptions. These obsidian occurrences are of secondary origin, with obsidian nodules spread over the surface.

**Ukraine (Carpathian III):** this obsidian location is situated in the Vihorlat-Gutin Mts. According to Dobosi (2011), obsidian is genetically linked to the fourth orogenic phase in the formation of these mountains, roughly contemporaneous with the Carpathian II obsidian. The primary obsidian source is located between Rokosovo and Malyj Rakovec in rhyolite tuffs. Dobosi (2011) states that the above mentioned three sources can be differentiated on the basis of age, geochemical features as well as physical properties like colour and transparency.

Obsidian is widely considered an ideal material for source tracing using elemental methods of analysis (Tykot, 2004). Many trace elements in obsidian are related to the gross composition of the parent magma. Many “incompatible” elements are not entering in early solid magmatic minerals, and accumulate in the liquid fraction of the magmas (e.g. Sr, Ba, Rb, Cs, La, Ce, Y, Ti, Zr, P, Ta, Nb, Be, B and Li). The evolving nature of magmas, which may incorporate country rocks during crystallization, results in changing patterns of absorption by different minerals. Both differential crustal contamination and fractional crystallization of the magmatic melt contribute to create considerable differences in the concentrations of the incompatible elements in volcanic flows, and these elements are thus particularly useful for obsidian provenance studies. Although surface water can exchange Sr, Na, K and other elements with the volcanic glasses, this effect is much more pronounced in devitrified glass or volcanic ash than in obsidian. Despite the advances in obsidian hydration dating (Friedman et al., 1997), many archaeometrists - e.g. Tykot (2004) – consider the discrepancies between geological specimens and archaeological artifacts deposited under different environmental conditions for the last several thousand years insignificant.

As mentioned by Tykot (2004), the first successful provenance study of Mediterranean obsidians relied on trace elements (Ba, Zr, Nb, Y) measured by optical emission spectroscopy. In Romania, our previous work used as provenance fingerprints rubidium, zirconium, barium, cerium, titanium, and manganese, measured by PIXE and XRF (Constantinescu et al., 2002), and rubidium, zirconium, titanium, manganese measured by milli-PIXE (Constantinescu et al., 2014). For Southern Italy, rubidium, strontium, zirconiums, measured by PIXE were used by Quarta et al. (2011).

### Materials and methods

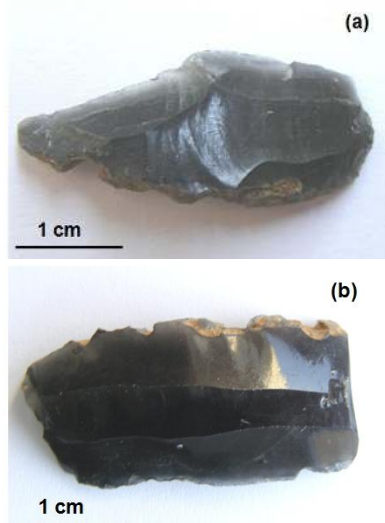
Archaeological samples i.e. Neolithic obsidian tools (Fig. 2) were obtained from “Țara Crișurilor” Museum, Oradea, Transylvania’s History National Museum, Cluj-Napoca and from Institute of Archaeology “Vasile Pârvan”, Bucharest. The studied samples are from archaeological sites within Oradea region (Seleuș, Bucin, Tașad), Cluj area (Iclod, Țaga, Turda, Silagiu), Iron Gates on Danube area (Cuina Turcului) and Teleorman area near Danube (Măgura). Geological obsidian samples originate in Hungary (Tokaj Mts.), Slovakia (Vinicki, Tokaj Mts.), Melos Island (Greek Island – Aegean Sea), Armenia (Aragats and Jerevan), Lipari, India, Arizona, Mexico (Teotihuacan) and Peru were also analyzed (Fig. 3). Both archaeological and geological samples were analyzed using XRF and milli-PIXE.

XRF measurements were performed using X-MET-TX3000 portable spectrometer with the X-ray beam generated by a 40 kV – Rh anode tube. The detection system is a PIN silicon diode detector with Peltier cooling. The resolution of the detector is 270 eV for the  $K_{\alpha}$  line of Mn (5.89 keV). The measurement spot size is about 30 mm<sup>2</sup>. The spectrometer has a Hewlett-Packard (HP) iPAQ personal data assistant (PDA) for software management and data storage.

Milli-PIXE measurements were performed at the 5 MV Van de Graaff accelerator of the Institute of Particle and Nuclear Physics, Wigner Research Centre of the Hungarian Academy of Sciences. The properly collimated proton beam of 3 MeV energy was extracted from the evacuated beam line to air through a 7.5  $\mu$ m thick Kapton foil. A target-window distance of 10 mm was chosen where the beam diameter was found to be about 1 mm. For the analyses the external beam intensity was varied from 1 to 10 nA depending on the actual total X-ray count rate. The obsidians were fixed to a micro-manipulator allowing for an accurate three-dimensional positioning. The final target positioning was achieved using a mechanical “aiming pin pointer”. X-ray spectra were collected by using a computer controlled Amptek X-123 spectrometer with an SDD type detector of 25 mm<sup>2</sup> x 500  $\mu$ m active volume and 8  $\mu$ m thick Be window. The detector with an energy resolution of 130 eV for the Mn  $K_{\alpha}$  line was positioned at 135°



with respect to the beam direction. The target-detector distance was 25 mm. The net X-ray peak intensities and concentrations were calculated subsequently with the GUPIX program package. In order to arrive at the final conclusions our PIXE results were compared to data from the literature obtained on samples from the same geological sources using different analytical techniques.



**Fig. 2.** Archaeological obsidian samples from Melos or Carpathian II type (a) and Carpathian I type (b).

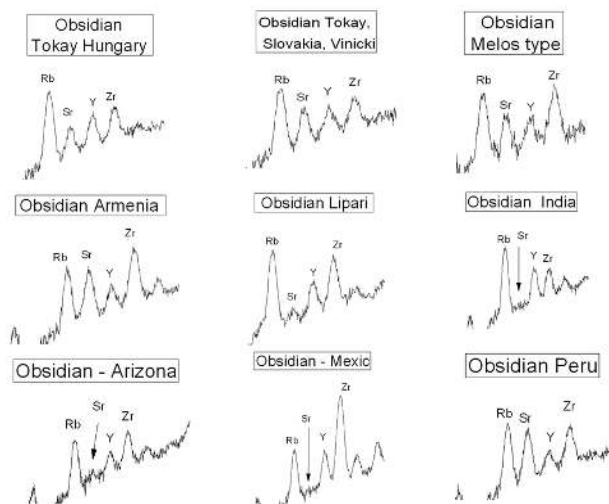


**Fig. 3.** Geological obsidian samples from Vinicki or Carpathian I (a) and Lipari (b).

## Results

The Rb-Sr-Y-Zr X-rays pattern is specific for each obsidian geological source (Fig. 4) and consequently it can be used as provenance marker.

To have a complete picture on the obsidian provenance in Prehistoric Romanian sites, archaeological samples from Iron Gates (Cuina Turcului site), Teleorman (Măgura site), Oradea and Cluj regions attributed to different prehistorical periods were analysed. Selected analytical results are presented in Fig. 5.



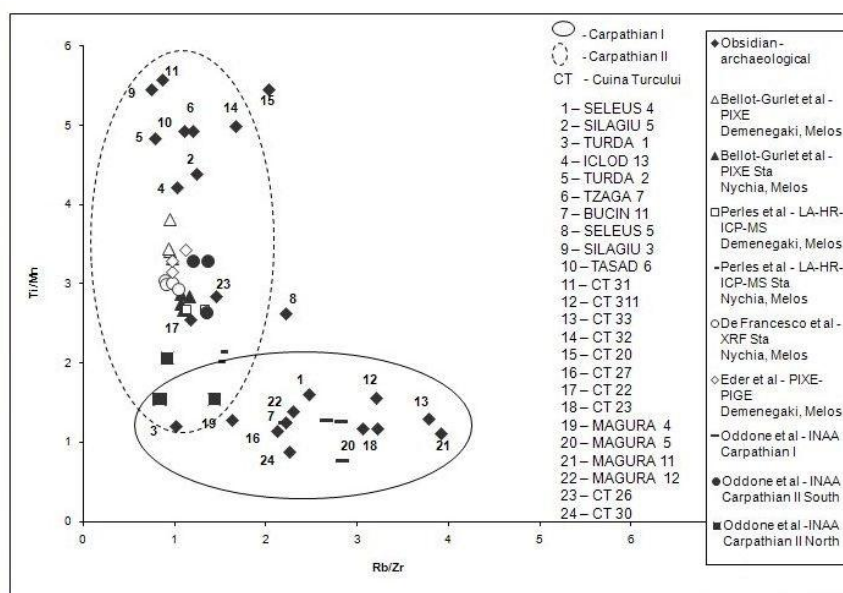
**Fig. 4.** Patterns of different obsidian geologic sources.

Data from previous works (Bellot-Gurlet et al., 2008; Perles et al., 2011; De Francesco et al., 2008; Eder et al., 2011; Oddone et al., 1999) and our data (XRF and milli-PIXE) were projected in a dimensional scatter plot of Ti/Mn versus Rb/Zr (Fig. 5). As shown in this figure the majority of Transylvanian Neolithic samples fit the Carpathian II pattern excepting Seleus 4 and Bucin 11. The Carpathian I pattern can be attributed to the Neolithisation period samples both for Cuina Turcului (CT311, CT33, CT27, CT23, CT30) and Măgura (Magura 4, Magura 5, Magura 11, Magura 12). For Cuina Turcului Mesolithic samples CT22, CT26, CT32, CT 31, and CT20 the situation is special, they could fit Carpathian II pattern but two of them are close to Melos

values, so, more samples from this category must be analyzed and an archaeological discussion is necessary. On the basis of our classifications, the majority of the Transylvania's obsidian prehistoric tools both from Cluj and Oradea areas were determined as coming from Hungarian Tokaj Mountains – Carpathian II pattern.

## Conclusion

Our study demonstrates that minor and trace elements as Rb, Sr, Y, Zr, Ti, Mn, can be successfully used to determine the provenance of archaeological obsidian, i. e. to identify the geological obsidian deposits.



**Fig. 5.** Scatter plot of Ti/Mn versus Rb/Zr ratios. The numbered points represent the results of the present work, the sources of the other data and the analytical techniques used are listed on the right side of the figure.

## Acknowledgements

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## FOURIER-TRANSFORM INFRARED SPECTROSCOPY (FT-IR) AND X-RAY DIFFRACTOMETRY (XRD) AS METHODS FOR DISCRIMINATING AMBER AND AMBER-LIKE MATERIALS FROM THE ROMANIAN MARKET

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**Abstract.** Amber and amber-like material are often found our days in the Romanian gemstone exhibitions. Fake amber is more and more difficult to detect, because modern manufactured products made of natural resins and/or polymers are so perfect, that they can produce same esthetic effects of the transparent and colored-like amber pieces. Macroscopically, they can not be separated from amber without a good personal experience or only applying gemological classic tests. So, modern physico-chemical methods, as Fourier transform infrared spectroscopy (FT-IR) and X-ray diffractometry (XRD) are applied, for discriminating amber and forgeries.

**Key words:** Baltic amber, romanite, copal, rosin, modern resins, Romanian gemstone market, Fourier Transform Infrared spectroscopy, X-ray diffraction, ageing study

### 1. INTRODUCTION

In Romania amber is treated as gemstone, including both commercial advantages and the risk of fake industry. Watching the gemstones events, shows and exhibitions organised in Romania especially after the 2000's, obviously raw amber and amber products are highly desirable. A large number of European amber varieties are exposed, both raw amber for the needs of manufacture or for the collectors, and amber objects: necklaces, pendants, pearls, islamic rosaries, earrings and finger rings with silver. Amber art is installed for good on the Romanian market, most of the objects being jewellery and religious creations. A larger project started in 2010, with the aim of establish the amber varieties and amber-like materials found on the Romanian gems market applying analytical techniques (Fourier Transform Infrared spectroscopy and X-ray diffraction). Gems from the exhibitions organized by the Geological Institute of Romania (GIR) (2011-2013) (Fig. 5, 8), Museum of Mineralogy in Baia Mare (MMBM) (2013) (Fig. 1), Museum of Gold in Brad (MGB) (Fig. 2, 5), from a gift shop from Bucharest (2012) (Fig. 4, 6), and amber gems given by a popular mineralogical magazine (2012) (Fig. 3) were included in this study. In all investigated situations, amber-like material was sold or just exhibited as worldwide genuine amber varieties, *e.g.*, Baltic Countries, Poland, Ukraine, Russia, Romania, Dominican Republic, Italy, Brazil, Myanmar, or as copal from Madagascar and Indonesia. Some interesting data have already been published, regarding discrimination of amber from substitutes, or the characterization of modified amber due to natural processes or 'gemological' treatments (Neacșu et al., 2010, 2013). Other information is referring to the relationship between the environment where resins, subfossil resins and amber have lain during the geological ages and the gemological properties of material, adding to previous studies of Neacșu and Dumitraș (2008). Finally, there is a special concern over ageing studies, which might contribute to a better understanding of degradation mechanisms of amber and amber-like materials used in gemology. The circumstances of ageing experiment show that visible light, atmospheric oxygen and the increase of air temperature give spectroscopic changes after three months (April, May and June 2012) consequently of free external atmospheric exposure of amber and angiosperm resins in the temperate-continental climate of Bucharest, Romania (Neacșu et al., 2014).

### II. EXPERIMENTAL PROCEDURES

Fourier Transform Infrared spectroscopy was performed in the Department of Mineralogy of the Faculty of Geology and Geophysics, University of Bucharest, using JASCO's FT-IR microscope system equipped with FT-IR 4100 spectrometer (DLATGS detector with Peltier temperature regulation, beam splitter substrate material Ge/KBr, resolution  $0.9\text{ cm}^{-1}$ , spectral range  $7,800\text{ to }350\text{ cm}^{-1}$ , Jasco software), and Irttronµ (IRT-1000) Microscope (objective mirror 8X cassegrain, manual exchange of objective with no alignment required, minimum measurement area  $100\text{ }\mu\text{m}^2$  DLATGS detector, sample observation area  $1.2\times0.9\text{ mm}$ ; independent X and Y variable aperture; ATOS). FT-IR absorbance spectra (FT-IRA) were recorded for this study. Infrared spectra were also recorded in Geological Institute of Romania, using a Bruker Tensor 27 FT-IR spectrometer, using ATR accessory (DTGS detector, KBr beamsplitter, spectral range  $7,500\text{ to }370\text{ cm}^{-1}$ , resolution  $\pm 1\text{ cm}^{-1}$ ,  $\pm 2\text{ cm}^{-1}$  OPUS software).

X-ray powder diffraction analyses were performed at the Geological Institute of Romania on a Bruker D8 Advanced automated diffractometer equipped with a graphite-diffracted beam monochromator (Cu  $K\alpha$  radiation,  $\lambda = 1.54056 \text{ \AA}$ ), at an operating voltage of 40 kV and a beam current of 40 mA.



Fig. 1. Baltic amber beads (MMBM).

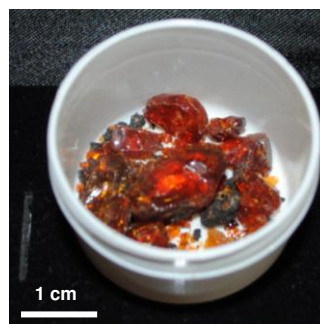


Fig. 2. Romanite samples (MGB).

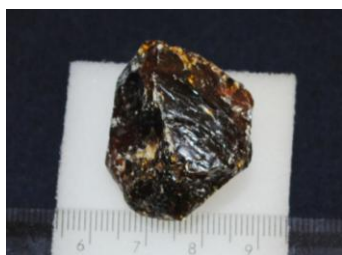


Fig. 3. Commercial "Indonesian copal" identified as rosin (scale in centimeters).

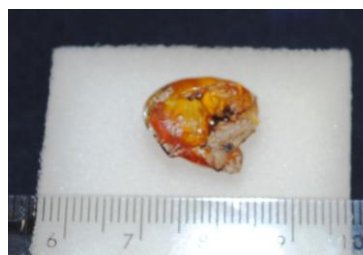


Fig. 4. Commercial amber identified as modern Angiosperm resin (scale in centimeters).

### III. RESULTS AND DISCUSSION

Fourier-transform infrared spectroscopy (FT-IR) and X-ray diffractometry (XRD) were employed on very small amounts of amber-like materials found as gemstone, art and religious objects, or different ornamental products, to look if they are natural or synthetic substitutes.

FT-IR absorbance spectra for amber-like samples are very similar to the previously reported by Beck et al. (1965), Kucharska and Kwiatkowski (1977), Kosmowska-Ceranowicz (1999), Banerjee et al. (1999), Pakutinskienne et al. (2007), Kosmowska-Ceranowicz and Wagner-Wysiecka (2013), allowing the identification of Romanite (RO) and Baltic amber (Fig. 5). Kosmowska-Ceranowicz (1999), Guiliano et al. (2007), Abduriyim et al. (2009), and Schollenbruch (2013), give additional information for copal identification (Fig. 8), which is sometimes identified by mistake with amber (Neacșu et al., 2013). Another unexpected surprise is the recent identification of burmite on the Romanian market (Fig. 7), based on spectral analysis of Kosmowska-Ceranowicz (1999). Modern resins are sometimes macroscopically identified as amber; consequently they could be sold as amber. After a comparison of their own spectral database and the atlas of Hummel and Scholl (1969), Neacșu et al. (2013) could identify Rosaceous resins as commercial 'amber' (Fig. 6). Based on the IR characterization of amber-like materials of Yoshihara (2009), rosin was identified after it was sold as Indonesian copal together with a popular mineralogical magazine.

There are few interesting regions on the IR spectra considered characteristic for amber in literature, consequently they are investigated for identifying amber and substitutes: near  $890 \text{ cm}^{-1}$ ,  $995 \pm 15 \text{ cm}^{-1}$ ,  $1250-1150 \pm 15 \text{ cm}^{-1}$ ,  $1375 \pm 5 \text{ cm}^{-1}$ ,  $1450 \pm 20 \text{ cm}^{-1}$ ,  $1600-1650 \text{ cm}^{-1}$ ,  $1735-1700 \text{ cm}^{-1}$ ,  $2962-2853 \pm 10 \text{ cm}^{-1}$ ,  $3048$ ,  $3095$  and  $3100-3700 \text{ cm}^{-1}$ . The  $3700-3100 \text{ cm}^{-1}$  region indicates a decrease of free water proportion to romanite in comparison with Baltic amber. The *fingerprints area* of Baltic amber presented the characteristic Baltic 'shoulder' ( $1250-1150 \text{ cm}^{-1}$ , -CO-O of succinate) (Beck et al., 1965, Pastorelli, 2009). IR analyses demonstrate that romanite has more carboxylic groups than Baltic amber (see the band of  $1735-1700 \text{ cm}^{-1}$ ,  $>C=O$  stretching of esters and acids, which increases in intensity to romanite) (Fig. 5). To distinguish amber from copal, the regions between  $1700-800 \text{ cm}^{-1}$  and  $3100-2800 \text{ cm}^{-1}$  are important (Fig. 8), where the vibrations of various C-O and C-H bonds, also C=C double bonds become visible (Schollenbruch, 2013). Our data show that the band  $1650-1600 \text{ cm}^{-1}$  related to  $>C=C<$  (non-conjugated) is missing at romanite, probably consequently to its geological origin (Neacșu, 2006). 'Modified amber' (ageing amber due to natural or artificial processes) and 'modified copal' (treated) could be identified among commercial amber objects, and described by Neacșu et al. (2013) based on the comparison of IR



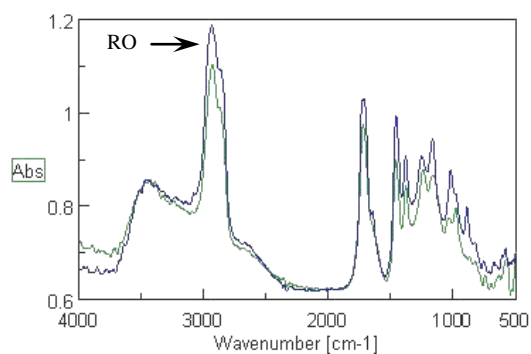


Fig. 5. The comparative FT-IRA spectra of amber identified as romanite (RO) and Baltic amber (GIR, MGB).

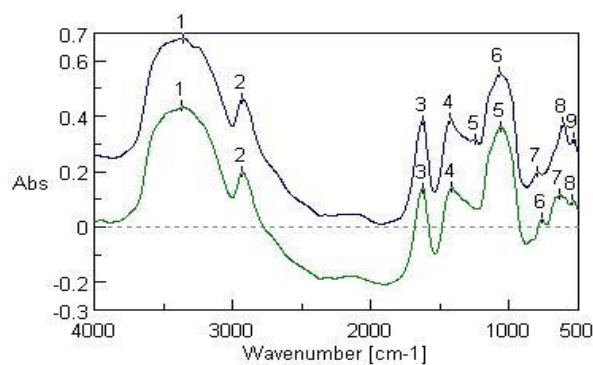


Fig. 6. FT-IRA spectra of commercial 'amber' identified as Rosaceous resins.

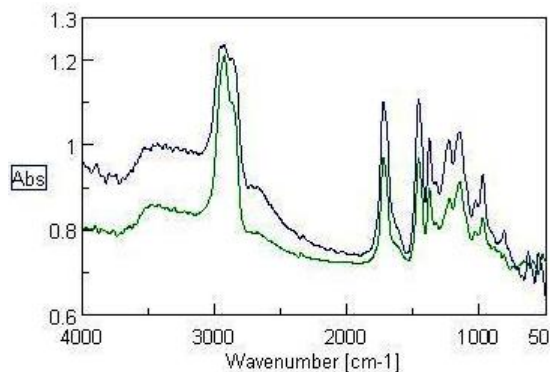


Fig. 7. FT-IRA spectra of amber identified as burmite (GIR).

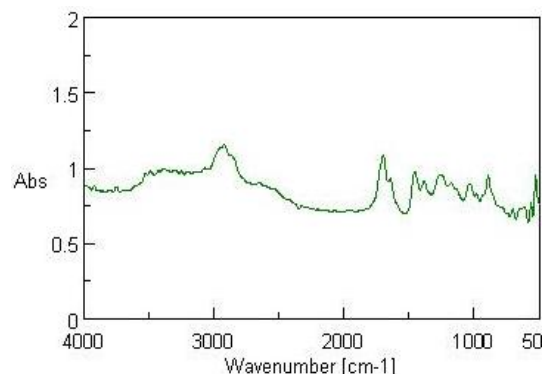


Fig. 8. FT-IRA spectrum of amber identified as Madagascar copal spectrum (Neacșu et al., 2013) (GIR).

spectral analysis with those of Pastorelli (2009), Kosmowska-Ceranowicz and Wagner-Wysiecka (2013), and Schollenbruch (2013). Also Dominican amber was identified, by confronting the FT-IRT spectra with those presented by Abduriyim et al. (2009), and Yoshihara et al. (2009).

In some cases, the records of amber-like materials exhibit the same XRD pattern as for Baltic amber, with a broad peak centered at  $2\theta \approx 15^\circ$ , indicating an amorphous state (Yoshihara et al., 2009) (Fig. 10). Some crystalline components of material *e.g.*, quartz, or the substitution of organic matter by minerals give rise to diffraction patterns in all spectra (Fig. 9).

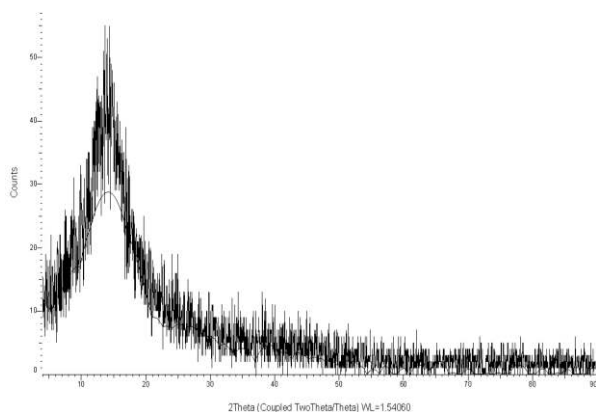


Fig. 9. X-ray diffraction of romanite (Neacșu et al., 2013)

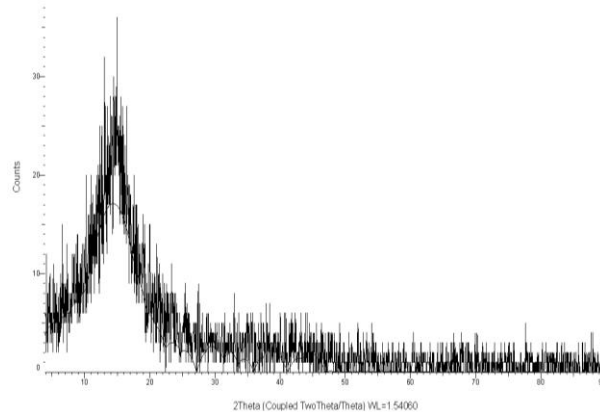


Fig.10. X-ray diffraction of Lithuanian amber (Neacșu et al., 2013)

These assumptions are confirmed by the microscopic studies of romanite and succinite (Neacșu, 2006; Neacșu & Dumitraș, 2008; Teodor et al., 2009; Neacșu, 2010 - [www.romanit.ro](http://www.romanit.ro)).

#### IV. CONCLUSIONS

None of the XRD records show any internal organizing tendency. These results contrast with previously published papers, where the XRD records indicate some internal organizing tendency for romanite, confirmed by the already mentioned microscopic studies. So, the possibility of using X-ray diffraction as a diagnostic method for romanite is not sustained for the moment.

All investigated materials presented FT-IR spectra that were compared with the already reported IR characteristic bands of amber and amber-like materials, confirming that this method is an excellent mean to detect fake amber. The IR analyses demonstrate that romanite has more carboxylic groups than Baltic amber, so romanite is strongly oxidized. The loss in C=C groups is an effect of maturation or ageing of amber (Shashoua et al., 2005). In sum, an older supposition that romanite could be ‘aged’ Baltic amber may be taken into consideration.

XRD remains a valuable complementary method, for revealing an internal organizing tendency of material, or minerals trapped inside it.

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## INDUSTRIAL DIAMOND APPLICATION IN CUTTING ORNAMENTAL ROCKS

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**Abstract:** Ways were looked for reducing synthetic diamonds consumption when cutting ornamental rocks (Topleț granite, Rușchița and Moneasa marble). Experiments performed with supertough ST diamonds embedded in different sintered metallic binders pointed to a better efficiency when using a Cu80-Sn20 bronze binder in comparison with a hard Widia type binder. For a better retention of the ST diamond crystals in the binder their perfect planar cube-octahedral faces have been corroded in an oxidizing fused NaNO<sub>3</sub> bath. The cutting behavior of the least perfect FM brittle diamond crystals embedded in a polymeric binder was improved by a surface treatment intended to envelop each crystal in a metallic Ni cage. SEM electron micrographs and cutting tests have attested the efficiency of both surface treatments.

**Key words:** saw grit synthetic diamonds, surface treatment of diamond crystals, improved retention in the binder

### Introduction

Diamond, the cubic variety of crystalline carbon, is the industrial mineral used in the smallest amount but with enormous economic benefits. The applications mainly come from the hardness of diamond which is the highest among all known substances. Its unique position comes from the type of hybridisation of the valence orbitals ( $2s^2p^2$ ) in carbon. As depicted in figure 1a four molecular orbitals (having identical energy and geometry) result when the unique 2s orbital and the three 2p orbitals ( $p_x, p_y, p_z$ ) of the carbon atom merge together. Thus, each carbon atom in diamond is bonded by four  $\sigma$  covalent bonds to its neighbors (figure 1b). The tetrahedral coordination is seen in the crystal structure of diamond (figure 1c). The covalent bonds in diamond are very strong as reflected by their short length equal to 0.154 nm (Petrescu and Fecioru, 2002; Petrescu, 2004).

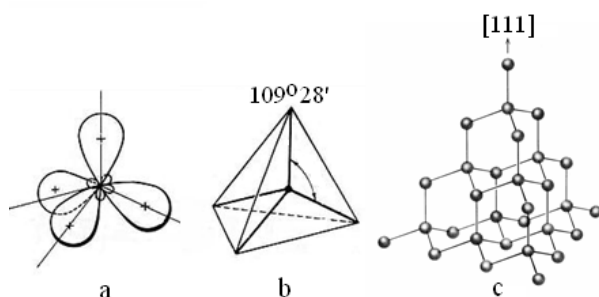


Fig. 1. a. Four degenerated  $sp^3$  orbitals; b. Tetrahedral coordination of carbon atoms; c. Diamond crystal structure

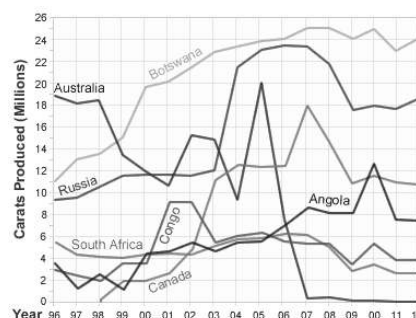


Fig. 2. Major diamond producing countries 1996-2012

About half of the natural diamonds from a total world production of 144 million carat or ~ 28.8 tons at 2010 level, according to United States Geological Survey Mineral Resources Program ([minerals.usgs.gov](http://minerals.usgs.gov)), are not suitable for gems and are of industrial grade. The main producers of natural diamonds in 2012, as listed by Geoscience News and Information ([Geology.com](http://Geology.com)) are Botswana, Russia, Canada, Angola, Congo, South Africa and Australia (figure 2). Since 1955 a new source became available for industrial diamonds, namely synthetic diamonds first put on the market by General Electric Comp. - USA. In 2010 the world production of synthetic diamonds reached an impressive value of 4380 million carat, from which 91% were produced in China ([indexmundi.com](http://indexmundi.com)). Since 1974 up to 2007 the RAMI Dacia Company in Romania was a producer of synthetic diamonds (micropowders and saw-grit type) and a producer of diamond inserted cutting tools.

As synthetic diamonds are identical in structure and properties to natural diamonds and as the raw material for their synthesis is graphite (a largely available material), prospects exist of sure and unlimited supply of synthetic diamonds for industrial applications. High-grade saw grit synthetic diamonds (up to 700 micron size) for cutting tools are industrially made by high pressure - high temperature synthesis (about 5 GPa and 1300°C). In such conditions graphite undergoes a reconstructive allotropic transformation and changes its simple hexagonal crystal lattice into a diamond cubic lattice accompanied by a change in hybridization of the valence electrons from  $sp^2$  to  $sp^3$ . To lower the pressure-temperature

parameters at reasonable levels metallic catalysts are used in the industrial process. A liquid solvent consisting of transition metals (Fe, Ni, Co) dissolves the graphite crystals and re-precipitates the diamond crystals. The catalytic role of the metallic solvent is mainly exerted by lowering the surface tension in the nucleation and growth process of diamond.

Due to their hardness industrial diamonds find application in drilling hard rocks in mining and oil extraction as well as cutting hard materials such as reinforced concrete or ornamental rocks (Wilks and Wilks, 1994).

This paper contains experiments performed with view to achieving the best use of synthetic diamonds when cutting ornamental stones (granite and marble) with minimum consumption of saw grit diamonds whose price is very high (tens of \$ per gram). Marble and granite have been cut in blocks or carved in statues since ancient times but what is new with diamond tools is the possibility of high speed cutting and polishing of large and thin marble and granite tiles for buildings facades and floors whose luster lasts for ever. This is done by using cutting disks provided with diamond inserted segments instead of metallic tools. The experiments in this paper were carried out with various binders (metallic or polymeric) for embedding diamond crystals in the cutting segments, as well as with various surface treatments applied to synthetic diamond crystals in view of improving their retention in the binder.

## Results and Discussion

Synthetic diamonds produced in Romania have been used in this research. Their shape perfection is depicted in the series of SEM electron micrographs in figure 3 (recorded by means of a Tesla 300 instrument). For each class we have measured the toughness expressed as percentage of unbroken diamond crystals after subjecting a 50 carat sample (1carat=0.2 g) to 2kg/cm<sup>2</sup> striking force (by means of a RO-TAP instrument). The experimental results presented in the legend of figure 3 show that decreasing the shape perfection from ST class to the least perfect FM class decreases the toughness and increases the friability by ~four times.

A first run of experiments has been carried out in view of evaluating the efficiency of the cutting segments as well as their consumption in the cutting process of various sorts of ornamental rocks (granite from the Topleț quarry, marble from the Rușchița quarry, marble from the Moneasa quarry). The cutting segments have been fabricated by embedding the synthetic saw grit diamond crystals in two different powder binders, denoted BR80 (consisting of a two phase bronze 80Cu+20Sn) or A10 consisting of a Widia type alloy (90% WC + 10% Co). With view to the harsh conditions during sintering the binder powders (600-1000°C) the best diamonds class ST have been used. The segments were 7 mm in height and have been mounted on the periphery of the cutting disk working at 30 m/s peripheric speed and constant power (~0.35 kW). The results in figure 4a and figure 4b point to a correlation between the type of binder and the type of processed ornamental rock. Figure 4a shows that the wear of the diamond inserted tool is lower when using the Widia type sintered binder (A10) than when using the sintered bronze binder (BR80) for all processed rocks. This is so because the A10 binder is itself very hard and wears less than the softer BR80 binder. However, as shown in figure 4b, the efficiency of the cutting process points to just the reverse behavior. When using the hard A10 binder the cutting efficiency is lower for all investigated ornamental rocks in comparison with the softer BR80 binder. This is an indication that the softer BR80 binder erodes itself in the proper manner to keep the diamond crystals in place until they become completely blunt and this is the best way to take the maximum benefit from the diamond crystals. On the contrary the poorer efficiency when using the hard A10 binder may be associated with a less proper erosion rate resulting in the blunt diamond crystals not being properly removed out of the binder matrix. Experimental data in figure 4b shows the influence of the mineralogical nature of the processed ornamental rock on the cutting efficiency when the optimum binder (namely BR80) is used. Expectedly, the efficiency when cutting hard granite is lower than when cutting softer marble. The difference in behaviour between Moneasa marble and Rușchița marble may be eventually ascribed to their different degree of metamorphism and texture, the Rușchița marble being especially compact and showing a sugar-like texture (Brana et al., 1986).

A second series of experiments was concerned with improving the retention of the ST diamond crystals in the best binder (BR80). Because the bond between the diamond crystals and the binder is not chemical but mechanical (interlocking mechanism) there is a risk for the ST crystals with very smooth faces (see figure 3) to be prematurely pulled out before they become blunt. To obtain a certain roughness of their surface we have applied a surface treatment consisting in immersion of the diamond crystals in a molten salt bath (NaNO<sub>3</sub> at temperatures higher than 500°C). In the electron micrograph in figure 5a we shown how the original perfectly smooth face of a diamond crystal class ST (see figure 3) has become rugged as



a result of the oxidation process promoted by the decomposition of  $\text{NaNO}_3$ . This demonstrates that the diamond surface can be etched (Pipkin, 1980; Nishibayashi, 1993). As seen in figure 5b the better retention of the corroded diamond crystals is clearly benefic for the cutting process.

Our results show that the oxidation-corrosion process is accompanied by a loss in weight (figure 6a) and a decrease in toughness (figure 6b) for the ST diamonds subjected to this surface treatment. Both these undesirable phenomena become worse when the temperature of the molten salt bath and the time of immersion are higher. We have succeeded to minimize these phenomena by an addition of anhydrous  $\text{NaOH}$  to the molten  $\text{NaNO}_3$  bath as clearly indicated by the results in figure 6a and figure 6b. When optimizing the physical and chemical process parameters of this surface treatment one has to take into account the high price of the diamond crystals and not let the diamond losses exceed a value higher than  $\sim 2.5\%$ .

A last set of experiments was concerned with synthetic diamond crystals embedded in a polymeric binder, i.e. an Epoxi type resin. Such cutting tools are intended to work in less severe machining condition diamonds of inferior quality (class FM) were used.

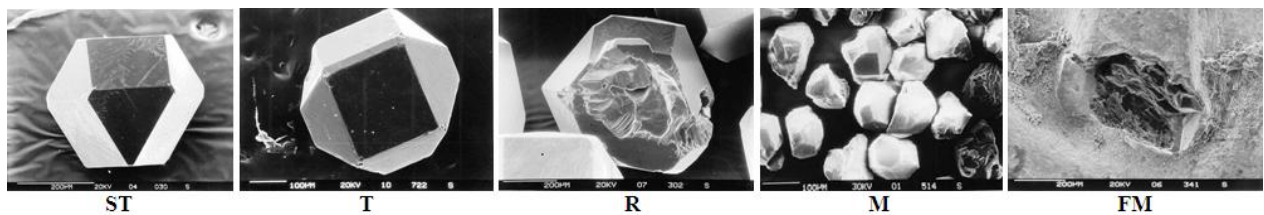


Fig.3. SEM micrographs:

ST - supertough diamond crystal; smooth and perfect cube-octahedral faces (toughness 95.5%)

T - tough diamond crystals; small imperfections on the cube-octahedral faces (toughness 88%)

R - class: large imperfections on some cube-octahedral faces (toughness 56%)

M- class: poorly developed cube octahedral faces, rounded edges, rough faces (toughness 40%)

FM - class: irregular shape, very rough faces (toughness 22%)

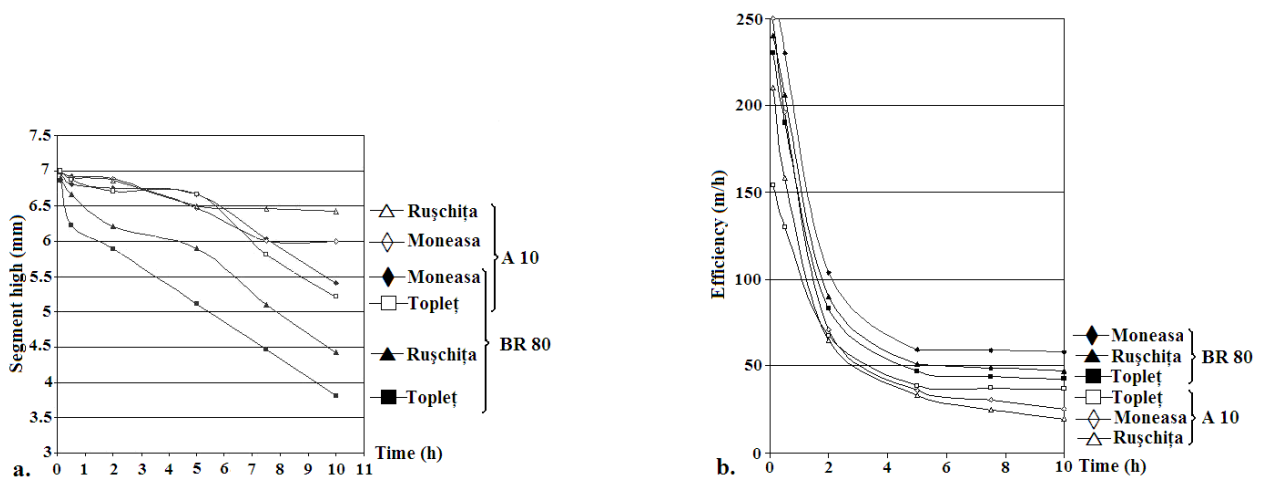


Fig.4. Experimental data on cutting Topleț granite, Ruşchița and Moneasa marble: a. Tool consumption estimated from the height of the cutting segment (original height  $h = 7$  mm); b. Cutting efficiency  $\eta$  (mm/h) versus cutting time

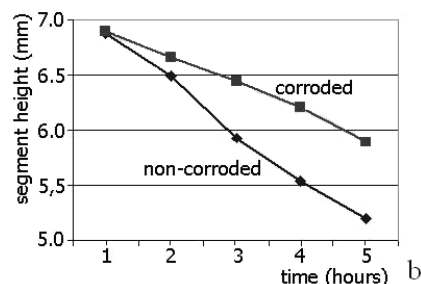
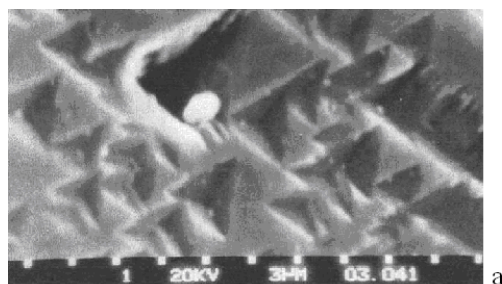


Fig.5. a. SEM micrograph of a corroded crystal face; b. improved wear resistance of cutting segments (Ruşchița marble)

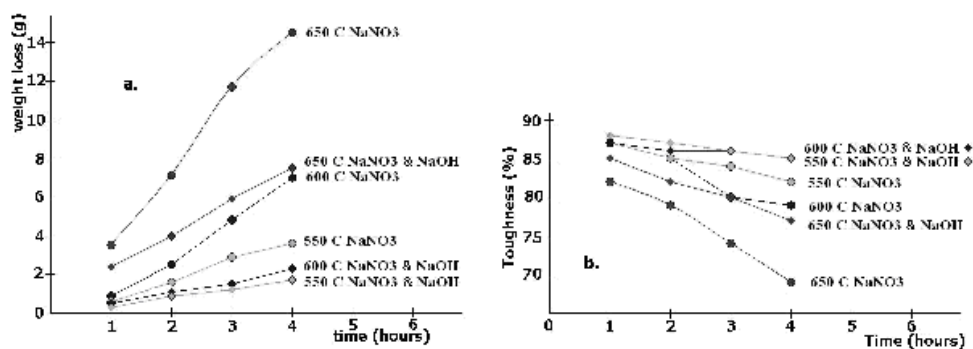


Fig.6. Weight losses (a) and toughness decrease (b) for a 200 carat sample of ST diamond crystals during corrosion

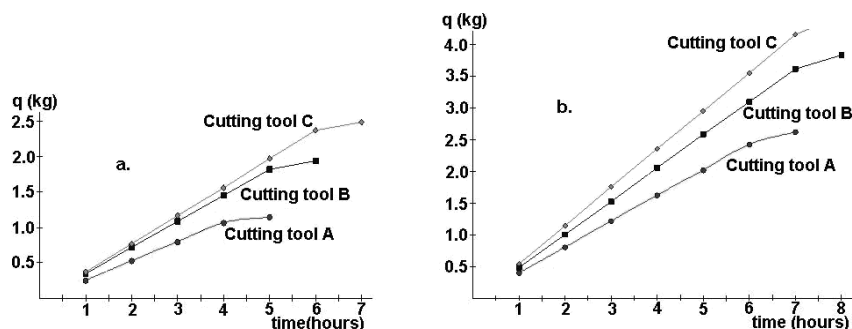


Fig.7. Cutting efficiency expressed by cumulated amount  $q$  of processed Topleț granite (a) and Rușchița marble (b)

Diamonds used in these tools are friable (toughness ~22%), but a cage of electrolytic Ni deposited on each crystal is a good solution. The surface of such Ni coated diamond crystals and it proved to be very smooth under SEM. We inferred that this is detrimental to a good retention of the diamond crystals in the binder and carried out experiments to obtain a corrugated Ni cage. This was accomplished by combining the electrolytic deposition of Ni (95%) with its chemical deposition (5%). As seen in figure 7 which compares the cutting efficiency when using non-coated FM diamond crystals (tool A), 100% electrolytically coated (tool B) and 95% electrolytic +5% chemically coated diamond crystals (tool C) the new procedure proved to be successful.

## Conclusions

A quantitative correlation has been established between diamond crystal perfection (revealed by SEM electron examination) and toughness. Cutting tests have indicated the superiority of a 80Cu+20Sn sintered bronze binder over a Widia type (90WC+10Co) sintered binder when diamond inserted cutting segments were used for machining Topleț granite, Rușchița and Moneasa marble. The cutting efficiency of supertough diamond crystals embedded in 80Cu+20Sn sintered bronze binder was greatly increased by an oxidative surface corrosion of the diamond crystals intended to improve their retention in the binder. For less perfect diamond crystals embedded in a polymeric binder a surface treatment consisting in encapsulating each diamond crystal in a Ni cage produced by electrolytic/chemical deposition proved to be benefic.

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## AGGREGATES PLANNING – TOWARDS A NEW VISION OF MINERAL RESOURCES

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**Abstract:** Aggregates represent an engine of the economy. Almost 65% of the aggregates consumed in Europe annually are used for building construction purpose. Aggregate production in Europe comes from quarries and pits. European demand for aggregate will reach more than 3 billion tons in the medium term in central and South Eastern Europe. In Romania, in 2012, there were 17 types of substances with 469 active and waiting licenses. The main activities related to aggregate production are the exploitation in quarries and pits and the processing of the extracted material. Quarrying management of the aggregates require a permanent equilibrium between pre-set regulations, adapting to the local realities and the initiative of local operators of the quarry being worked. Many of the countries within European Union have elaborated mineral plans in aggregate industry, a practice that should be adopted at a regional scale.

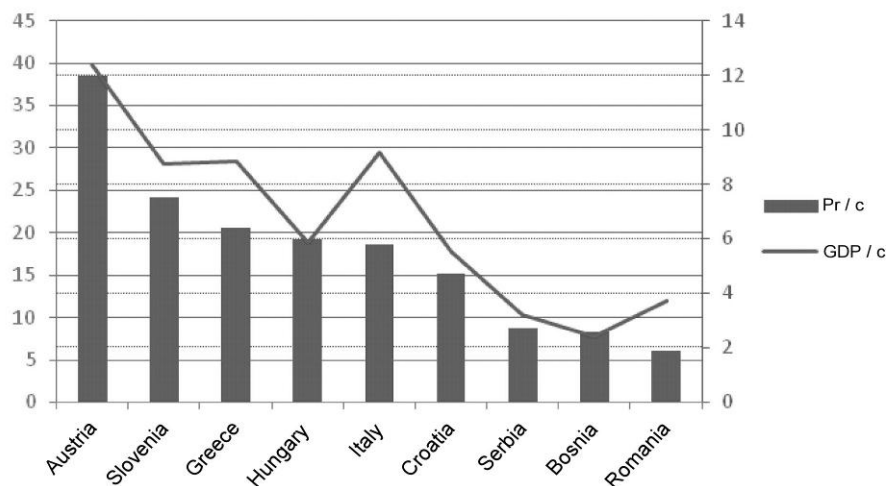
**Keywords:** aggregates, resources, sustainable management, planning

### I. Introduction. Importance of aggregates in Europe

Without any doubt, the aggregates can be considered the star of non-metallic mineral resources and representative of the most usable resources in the construction of buildings, roads and other infrastructure facilities. The production of aggregates represents an engine of the economy and a factor of living standard.

Almost 65% of the aggregates consumed in Europe annually are used for building construction purposes. Some 90% of the overall aggregates production in Europe comes from quarries and pits. Other remaining 10% of the European aggregates production comes from marine deposits and recycling of industrial waste (UEPG report, 2011). 30,000 tons of aggregates are needed for the overall construction of 1 km of a national scale road. Quantities corresponding to 20% of the European consumption of aggregates refer to construction of the road surface, runways, railways and waterways ([www.sarmaproject.eu](http://www.sarmaproject.eu)).

Despite society dependence on natural aggregate, urban expansion often works to the detriment of the production of those essential raw materials (Solar et al., 2004). In the advanced economies of Europe, the annual aggregates demand reaches 12 tons per capita. The sector suffered under the economic crisis since 2009, but, from 2012, increased again. European demand for aggregates will reach more than 3 billion tons in the medium term, driven mainly by economic growth in *Central and South-Eastern Europe* (Fig.1).



**Figure 1.** Aggregates production in South-East Europe in 2011- tones/capita and GDP (Source: UEPG Report 2011)

## II. Conditions available in the aggregates industry. Case study Romania

In 2000, in Romania, a country with a complex geological structure, there were over 750 known deposits of natural aggregates. The placement of the exploitation and/or processing of stone units or concrete and prefabricates factories is equilibrated relative to the national territory, with maximum 120 km to the initial deposit. In 2012, there were 16 types of substances with quarries of crushed stones ([www.namr.ro](http://www.namr.ro)): *amphibolite, andesite, basalt, limestone, dacite, diabase, diorite, dolomite, granite, granodiorite, sandstone, micashist /gneiss, porphyries, serpentinite, green shists, tuffs and pits of sand and gravel* - table 1.

**Table 1.** Situation of the licenses for aggregates extraction in Romania currently and potentially available

Types of licenses	Crushed stone	Sand and gravel
<b>Active</b> licenses (current resources)	<b>101</b>	<b>224</b>
Licenses waiting approval (potentially available)	162	245
<b>TOTAL</b>	<b>263</b>	<b>469</b>

## III. Best practices in aggregates industry of South Europe countries

Although there is not widespread, the waste aggregate production began to be practiced at increasingly large scale, even in South East Europe (Blengini et. al, 2013). For the production of aggregates in Europe some conditions need to be met:

- Sand, gravel or rock must exist in sufficient quantity to make mining worthwhile and must be accessible;
- The property must be of sufficient size to locate a pit or quarry and processing equipment and be owned by a person or company;
- The deposit must physically be able to be mined without causing unacceptable impacts to the environment;
- The exploitation can take place without adversely affecting the environment or lifestyle of people;
- The operation must be profitable considering all costs: exploration, environmental controls and transport.

The best practice for aggregates production applied in South East Europe countries are the exploitation in quarries (often in strip banding quarries, see Fig. 2) and pits and processing of the material. Crushed stone and sand and gravel commonly are obtained from dry pits or quarries, but in some setting may be mined from water - filled excavations using dredges mounted on barges or with draglines.

The crushed rock production activity involves infrastructure works on-site and off-site ([www.sarmaproject.eu](http://www.sarmaproject.eu)), development of quarry structure, extraction of rock, necessary after blasting, crushing and sieving, storage and transportation of the final products to market. Sand and gravel deposits are exploited with excavators after removal of the soil cover and by dredging below the aquifer level. After this distribution occur automatically sorts and sizes of aggregates required by the market.

Most of production from Romania (100 Mt, slightly less than 10-11 years ago), and generally in South East Europe take place in pits utilizing earth-moving equipment. Mining crushed-stone generally requires drilling and blasting of solid bedrock which breaks the rock into rubble of a size suitable for crushing and often has a negative impact on the environment (Fig. 3).

In the last years, the use of the secondary and recycled aggregates was promoted, especially in the west European countries. However, only when it is proved that the recovery /recycling process is both economically and environmentally sustainable, in comparison with the use of natural aggregates, the contribution of recycled aggregates can be considered net positive (Blengini et al., 2013).

Reclaiming aggregates operations or quarried sites has very high potential to improve the quality of life, create wealth, increase biodiversity and restore the environment. Today, fulfilling demand for an increasing aggregate exploiting requires ([www.sarmaproject.eu](http://www.sarmaproject.eu), [www.snapsee.eu](http://www.snapsee.eu)):

- Efficient and sustainable supply chain (planning, extraction, transport, use and recycling);
- Socio-ecofriendly quarrying and planning aggregate vision.

The recovery of quarries means the multiplicity of desirable and feasible actions and objectives that favor the restoration of the natural equilibrium in the belonging territorial areas ([www.sarmaproject.eu](http://www.sarmaproject.eu)). To limit the negative impact of the mining works in the plans of development,



Figure 2. Limestone aggregates Quarry from Slovenia, which uses strip banded method.



Figure 3. Dacite quarry from Cluj County, Romania, with environmental impact because of the slope found operating

the environment management of the companies must provide a number of measures of best practices (Marica and Bindea, 2011). These include the necessary elements for a completely safe working from the point of view of the protection and monitoring of the deposit, of labor and environment protection.

#### **IV. Role of sustainable management of aggregates in aggregate planning**

Sustainable aggregates resource management is an approach that supports development of policies, which reflects good science in operations, public preferences and financial and social constraints (Solar et al., 2004; [www.sarmaproject.eu](http://www.sarmaproject.eu)). The management of exploitation and sustainable management of its resources require a complete knowledge from quarry design to its closure (Marica and Bindea, 2011).

Quarrying management requires a permanent equilibrium between pre-set regulation, adapting to the local realities and the initiative of local operators of the quarry being worked. The environment management system aims at supporting carrying out of all the industrial processes within an organization in accordance with the European norm Standard ISO 14001, in view of supplying elements of a new efficient management system, structured and integrated in the global management activities of the company in question.

Main objectives of the sustainable aggregates management should be the supply security and resources efficiency ([www.sarmaproject.eu](http://www.sarmaproject.eu)), which can be achieved by:

- Extraction of the maximum possible amount of aggregates from a deposit;
- Use of the extracted aggregates for the most valuable application with respect to the aggregates quality;

- Tuning royalties and fees and fees on quarries to harmonize them with the surrounding areas and promote re-use, recycling and efficient transportation

At the same time, it is necessary to increase knowledge of potential impact on local communities. The aggregate industry needs to have access primarily to local resources. Access to land is in European countries (increasingly in some SEE countries) limited not to geological reason but due to non-existing land –use management principles related to aggregates ([www.sarmaproject.eu](http://www.sarmaproject.eu)).

## V. Aggregate planning and the future in mineral resources

A minerals policy may be defined as a policy to secure the supply of the economy with mineral resources by the entirety of action that a state can take to influence the supply of mineral resources on its territory and beyond (Tiess, 2011). A national aggregates policy framework should include/provide a mineral statement, objectives, strategies and action plan. Several countries within the European Union (United Kingdom, Finland, Austria) have elaborated national mineral plans in the aggregate industry and for all minerals in general, as key sectors contributing to jobs, wealth and a high quality of life for their citizens. An innovative approach of the sustainable resource management and a defined plan inclusive of Sustainable Supply Mix (SSM – SARMa Manual, 2011) is that it aims to ensure the supply with aggregates resources on one hand as well as to improve efficiency and solve the problems of land use on the other hand. In such terms it is important to use the recycled aggregates (Blengini et al., 2013).

In order to achieve transparency, stability and security for all concerned stakeholders of the aggregates exploitation and supply chain, a necessary part of the each country mineral policy framework has to be transferred in the regulatory framework where *the Community aggregates policy and minerals plans* are for the first priority plan. Through these concepts and future rules, a major role is the implementation of mineral planning in each country. Appropriate policies (including sectorial aggregates planning) are required to enable the balance between supply, production and environmental impact, infrastructure construction activities and climate protection ([www.snapsee.eu](http://www.snapsee.eu)).

These policies include: improvement of aggregates regulatory framework, clearly defined duties and responsibilities, ensure major, regulatory body for the South-East Europe countries, coordination between permitting procedure / authorities and land use planning management, strategic Environmental Impact Assessment, nature conservation issues, Public participation with encourage community consultation and involvement.

Demand forecasting is an important tool for establishing a mineral policy framework.

## VI. Conclusions

In the present, crushed stone and river aggregates are first rank mineral resources, considering the demand in the world and in Europe. The South Eastern European countries play an important role in aggregate industry.

The principal objectives of sustainable aggregate resource management and supply security are resources efficiency and environmental protection of post closure extracted areas.

Planning of primary and secondary aggregates in South East Europe countries must be carried out in an integrated way because demand for aggregates used in the construction industry depends on technical quality of products and end-uses.

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## UPDATED INVENTORY OF MINERAL NON-METALLIFEROUS AND NON-COMBUSTIBLE RAW MATERIALS EXPLOITATIONS OR PERIMETERS IN BIHOR COUNTY

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**Abstract:** The considerations which underlie the need of this work consisted in the regional economic development in Transylvania in the construction materials sector, by designing works presenting national interest (expansion or construction of highways, modernization of road lines, buildings) and the need to find solutions for re-training the work force or the implementation of the normative regulations. The paper presents the main non-metalliferous and non-combustible raw materials from Bihor county, covering not only dimension stone area, but also other industrial areas for finished products: construction ceramic, sanitary or fine ceramic, binder, glass, precast.

**Keywords:** Economic geology, Bihor county, mineral deposits, exploitation.

### INTRODUCTION

The present paper proposes an updated view on the mineral resources from Bihor county, in the context of an increasing demand for aggregates for roads or other different raw material for building industry, also for finding solutions for different demands of companies from industrial sector. The present stages of these were not detailed, because year by year a lot of changes are counting. This information can be found on the National Agency for Mineral Resources' portal, with active licences.

The main non-metalliferous and non-combustible raw materials from Bihor county cover not only dimension stone area, but also other industrial areas for finished products: construction ceramic, sanitary or fine ceramic, binder, glass, precast (Table 1, Fig.1). The inventory involves deposits with confirmed reserves with exploitation works, closed activity or just interest perimeters.

### 1. GENERAL FRAME

#### 1.1. Administrative aspects and access to the facilities

Bihor County, with an area of 7,535 square kilometres and its capital at Oradea, is connected by road from Romanian capital, Bucharest, from neighbouring counties, across the country and other European countries through railways and roads with 1-3 lanes. The main railway line connects the capital Bucharest with Central and Western Europe through Episcopia Bihor border point. The forest roads have also a significant role and facilitate the access to perimeters with useful rocks, deposits or quarries.

#### 1.2. Geographic and geological framework

*The mountainous territory* of Bihor County belongs to the Apuseni Mountains (Mutihac et al., 2007):

1. the Sub-group of the Bihariei Massive (including SW corner of Bihor Mountains and the W part of Vlădeasa mountains); the structural unit of Bihor presents a subdivision into blocks and supports the Western part of the Arieşeni and Biharea canvas;

The Bihor Mountains are made up of Palaeozoic and Mesozoic sedimentary deposits, covering an intensely fragmented epimetamorphic crystalline basement. Vlădeasa Mountains are made up of an important body of Banatite tephrolith (riolite, dacite, andesites, granodiorites and porphyries), which pierces the upper Cretaceous cover or merging with it.

2. the Sub-group of marginal horsts is a lowered mountainous step, filled with alternate molassic and Neogene deposits forming spurs which are extended to NW:

Codru-Moma Mountains - horst bordered on all sides by grabens, with a small granitic massif on the NW, a large cover of Permian deposits and Triassic dolomite limestone.

Pădurea Craiului Mountains - intensely fragmented and eroded horst, where the Mesozoic sedimentary deposits and the karst were formed before Neocomian. The karst has a great

extent and occupies a varied surface and underground relief (karstic sinkholes and depressions), to which bauxites are genetically related.

Plopiș Mountains (Lowlands) - made up of crystalline schists, belonging to the mesometamorphic series of Someș and to the epimetamorphic Arada series.

**The hills area** is part of the hilly units, developed on crystalline-Mesozoic formations, fractured on NW-SE and SW-NE directions, accompanied by volcanic massive, constituting the Western hills and depressions. They fall into Sylvania depressions and hills (Marghitei, Crișanei). The external front is found mostly on the NW side of the Plopiș Mountains and on the W part of Pădurea Craiului and Codru-Moma Mountains.

**The depression area** stretches to the W of hilly region, with altitudes between 200-300 m, forming Beișului, Vad - Borod and Barcău Depressions.

**The plain area** is represented by the high plain of Valea lui Mihai, Salontei, Crișurilor, Barcăului and Ierului Plains as part of the Western Plain, composed of a crystalline and sedimentary basement (from Palaeozoic to Palaeogene), with a changing cover composed of lacustrine deposits in the base and aluvio-proluviale at the top, and wind deposits.

## 2. CURRENT SITUATION OF MINING OF MINERAL SUBSTANCES IN BIHOR COUNTY

### 2.1 Prospecting / exploitation permits and explorations / exploitation licenses. Other legislation

An inventory made in the last decade in Romania have counted more than 400 deposits for building materials: aggregates and crushed stone, clayey resources for ceramic industry, dimension stone, stones for binders and others (Marica et al., 2008). According to the evidence from National Agency for Mineral Resources, 45 mineral substances are going to be extracted in 2014 in 328 quarries through exploitation licences and other 890 perimeters received exploitation permits for 1 year for 27 raw materials (except the waters and non-combustible materials).

From this total, almost 60 are located in Bihor county, including quarries, open pits or only as perspective areas (Brana et al., 1986), corresponding to 14 types of mineral non-ferrous and non-combustible resources (see Table 1). Most of them have extraction activity and official recording of the resources and reserves, but nowadays less than 30% develop exploitation works.

There are only 5 quarries for dimension stone from Bihor county included in the Romanian Annex (A.2.16) of European Standard for Denomination Criteria, SR EN12440:2008: Călugări - Ponoare, Câmp Vașcău and Lara - Câmp Moți for limestone, Pietroasa SE for granite/granodiorite and Vintere for sandstone (PROCIMA GEOLOGI, 2009).

### 2.2 Inventory of mineral resources and reserves exploitations and deposits

For a better understanding of economical values of resources in Bihor country, the deposits and perimeters were grouped and listed depending of their final use (Table 1).

## 3. CONCLUSIONS

The information presented in this article aims to contribute to the knowledge of updated mineral resources of the Bihor County by the regulatory bodies or those that promote territorial economic development, by investors or other different users of information for project proposals, through (Cetean et.al., 2006):

- structuring regional development programmes;
- the ranking of local opportunities to harness economic resources;
- presentation of general informative data in anticipation of the concession of deposits;
- establishing of the perspective perimeters by geological point of view, necessary to be explored and/or establishment of the current economic and technical conditions of use (Cetean et al., 2003);
- determining the opportunities for expansion of the areas of use of resources in order to increase the profitability of mining, as well as the quantification of the monitoring programmes and environmental restoration.



Table 1: Listing of perimeters with non-metalliferous and non-combustible mineral resources from Bihor County used for construction and sanitary industry

<b>DIMENSION STONE: internal and external paving, modular tiles, ornamental works etc.</b>	
Dacite	Șoimi
Granite, granodiorite	Brădișoru de Jos – Perim. II (Maidan), Pietroasa, Valea Lazului*
Limestone, marble	Băița Plai, Borz – V. Armanului*, Chișcău Deal, Chișcău – Pietroasa – Beiuș, Cresuia – Beiuș*, Ponoarele (Călugări) – Cărpinet, Șuncuiș, Tărcăița, Tărcăița – Valea Binselului – Cresuia, Valea Mare – Codru, Valea Mânioasa, Valea Seacă – Pietroasa, Vașcău – Câmp, Vașcău Câmp Moți Negaia, Vașcău Câmp Moți Sat
Quartzite	Șoimi, Teaca, Urviș – Coasta Morii*, Vintere
Amphibolite	Cuzap – Popești, Rezu Mare*
Sandstone, +/- conglomerate	Butan, Coasta Morii – Urviș, Huta – Șoimi, Urviș, Urviș – Coasta Morii, Vintere
Micaschist, gneiss	Bistra Gruiu*, Rezu Mare*, Suplacu de Barcău, Voivozi
<b>MINERAL RAW MATERIALS: crushed stone for road, railroad and buildings infrastructures, cement, binder, raw, semi-fine (sanitary) and fine ceramic (porcelain)</b>	
Industrial limestone	Aleșd (Aleșd – Subpiatră*, Fișca – Aleșd, Hotar – Aleșd), Aștileu – Valea Morilor, Aștileu - La Cruce, Băița Bihor*, Băița Plai, Banlaca – Dl Magheruș, Betfia, Borzi, Bratca, Brătești*, Budureasa, Călugări, Cărpinet*, Câmp, Colești, Corbilor, Coșdeni - Pomezueu, Criștior, Hidiș - Pomezueu, Hidișelul de Sus, Hodiș, La Cruce, Lion*, Lorău, Moți, Peștiș, Peștera (Dl Corbilor), Ponor, Remeti, Șomlău, Șuncuiș, Uileac, Urviș (Dl. Osoiu, Dl. Călugăru), Vad (Vadu Crișului), Vașcău, Vida
Dolomite	Băița Bihor*, Bratca - Lorău, Valea Mare – Budureasa (dolomite/limestone with brucite)*
Refractory clay	Borlaca, Borodul Mare, Brates, Bratca, Butan - Aștileu (Dl. La Făgeți), Caramazan*, Dealul Crucii, Lorău, Șuncuiș (Banlaca – Șuncuiș*, Damiș, Dumbrava – Șuncuiș, Roșia Albioara, Recea – Rujet, Tău Roșu – Șuncuiș)
Common clay, /- marl	Aleșd (Hotar* +Facsă), Beiuș, Biharia*, Buteni, Calea Clujului, Ceica, Cordău, Dealul Craiului*, Dobrești, Episcopia Bihorului, Marghita, Saldabagiu, Șuncuiș – Dl. Simionului*, Oradea, Valea lui Mihai, Vad (Vadu Crișului), Valea Cristioarel*
Siliceous sand	Aleșd, Beiuș, Cetea, Cicfoiaș – Budișor, Episcopia Bihorului, Ineu, Oradea, Tinca, Valea lui Mihai – Șimian, Valea de Finaț*
Sand and gravel	Aleșd*, Batar – Tauț (R. Crișu Negru)*, Beiuș, Beiuș – Drăgănești, Bella*, Borș – Sântău*, Drăgănești – R. Crișul Pietros, Crișul Morii*, Daval Episcopia *, Episcopia Bihorului*, Finiș - Valea Ioanis*, Ineu*, Maredu*, Oradea, Poietari*, Ponoras*, Pradea - Sântăul Mic, Roșiori Barcău*, Sântandrei – Tărian*, Sântău – Valea Trandafirilor*, Sântăul Mic – Gavella*, Sântăul Mic – Simbac*, Șoimi, Tărian – Borș*, Tărian Nord*, Tileagd*, Tinăud (R. Crișul Repede), Tinca
<b>OTHER USES (jewellery, ornamental objects)</b>	
Aragonite	Șuncuiș

\* Open quarries and pits (48) in the evidence of National Agency for Mineral Resources for exploitation in 2014

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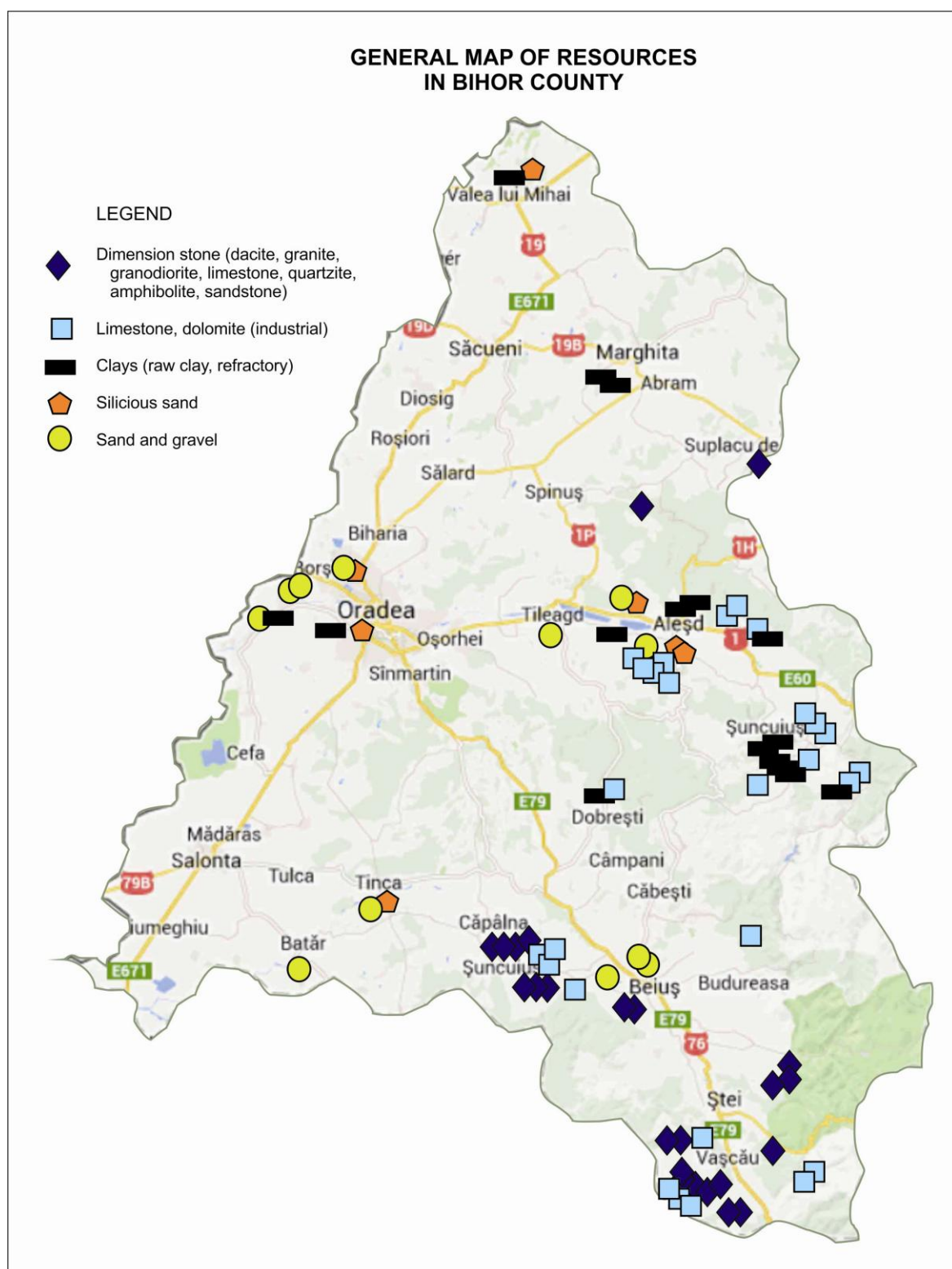


Fig.1. General location of non-metalliferous and non-combustible raw materials perimeters in Bihor county.

## GEOLOGY OF KIZILKAYA (SEVINÇLİ / AKSARAY) IGNIMBRITE AND INVESTIGATION OF THE USAGE AS BUILDING STONE (TURKEY)

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### Abstract

Aim of this study is to determine geologic, mineralogic-petrographic features and investigation of the usage building stone of the Kızılkaya ignimbrite outcropping around the Sevinçli (Aksaray) Town. For this purpose the geology of Kızılkaya ignimbrite were defined and mineralogic-petrographic properties were examined at the polarising microscope. In addition, in order to determine the physico-mechanical properties, testes were carried out from Kızılkaya ignimbrite. Lower Pliocene Kızılkaya ignimbrite is acidic in composition, represented by welded tuff and characteristic for pyroclastic flow unit. The Units were defined based on vitric tuff characteristics and vitrophyric porphyric texture using petrographic study. Quartz and plagioclase are phenoclasts. Fine grained biotite, hornblende and small amount of pyroxenes appears to be dispersed in volcanic glass. Volcanic glass shards are typical in the matrix. We done an experimental works, using uniaxial compressive strength of 9.81 MPa, flexural strength of 4.06 MPa and compressive strength after frost of 9.11 MPa. Density of 2.58 g/cm<sup>3</sup> was established. Considering the geological features, mineralogical-petrographical results, and the physico-mechanical properties of Kızılkaya ignimbrite, it was found to be suitable for interior works as a building material in flooring.

**Key Words:** Ignimbrite, physical-mechanical properties.

### 1.Introduction

The study area is in the Aksaray province which is located in the Central Anatolia Region (Figure 1). Studies on the usage of natural building blocks of ignimbrites around the Aksaray is extremely limited. In this study, the main purpose is to investigate mechanical and physical properties of Aksaray-Kızılkata ignimbrite which is covering large area around Aksaray.

### 2.Geology of the study area

The study area is located in Aksaray and covers the area between the Ürümüş plateau, Sevinçli and Boğazkaya village (Figure 2). In the study area metamorphic and magmatic rocks of the Central Anatolian Crystalline Complex crop out and these rocks were overlaid unconformably by younger sedimentary and volcanic rocks. Bozçaldağ and Tamadağ metamorphic rocks of the Central Anatolian basement is the oldest unit with Pre-Mesozoic metamorphic rocks which outcrops of north-east of Aksaray (Seymen et al.,1981a,b; Göncüoğlu et al., 1993). In Tamadağ the metamorphic rocks are represented by schists and gneisses which including metacarbonate and metapelite layers. Bozçaldağ metacarbonate rock is represented by gray–dun colored and coarse calcite crystals with a thick solid marble. The metamorphic rocks are cut by Upper Cretaceous gabbro, granite and granodiorite intrusive igneous rocks belonging to Central Anatolia granitoids. The igneous rocks are divided into two sub-units as Gücünkaya granitoids and Mamasun gabbros (Güllü et al., 2003). It is considered that the granitoids are Upper Cretaceous in age (Göncüoğlu et al., 1991). Upper Cretaceous Kızıltepe formation are unconformably overlying the basement rocks of metamorphic and igneous rock. This formation consists of conglomerate, sandstone and mudstone in alternation with loosely attached, lenticular and terrestrial-origin clastics. Oligo-Miocene in age Mezgit formation is unconformably overlain by the Kızıltepe Formation (Uçar et al., 2008). Mezgit formation consist of conglomerate, sandstone, mudstone and evaporites. It is considered that Mezgit formation was deposited in continental fluvial and temporary lakes environments (Uçar et al., 2008). Upper Miocene Uzunkaya formation unconformably rest on the



Fig.1. Location map of the studied area



Mezgit Formation as well as Kızılkaya ignimbrites that cover it unconformably. Bottom level begins with large size block material and towards the top continues as an alternation of coarse grained pebble and fine-grained sandstone which reflects high and low energy periods. The Kızılkaya Ignimbrites has been named by Beekman (1966) for the first time. It consist of white, off-white, light pink or gray in color and exhibits a columnar structure due to the cooling cracks developing in the vertical direction (Figure 3). The Kızılkaya ignimbrite is a product of acidic composition and show characteristic pyroclastic flow and welded tuff. Kızılkaya ignimbrite range in age between 4.9 to-  $5.5 \pm 0.2$  Ma according to K/Ar dating and correspond to Lower Pliocene (Batum, 1981). In the study area Quaternary alluvial sediments are also exposed in Ürümüş plateau and Keçeli area and consist of volcanic-origin of fine grained silt and clay materials. Actual Quaternary alluvial deposits consist of unconsolidated sand and gravel material. This unit outcrop in the Aksaray plain, Hamamboğazı creek and in the Ulurmak.

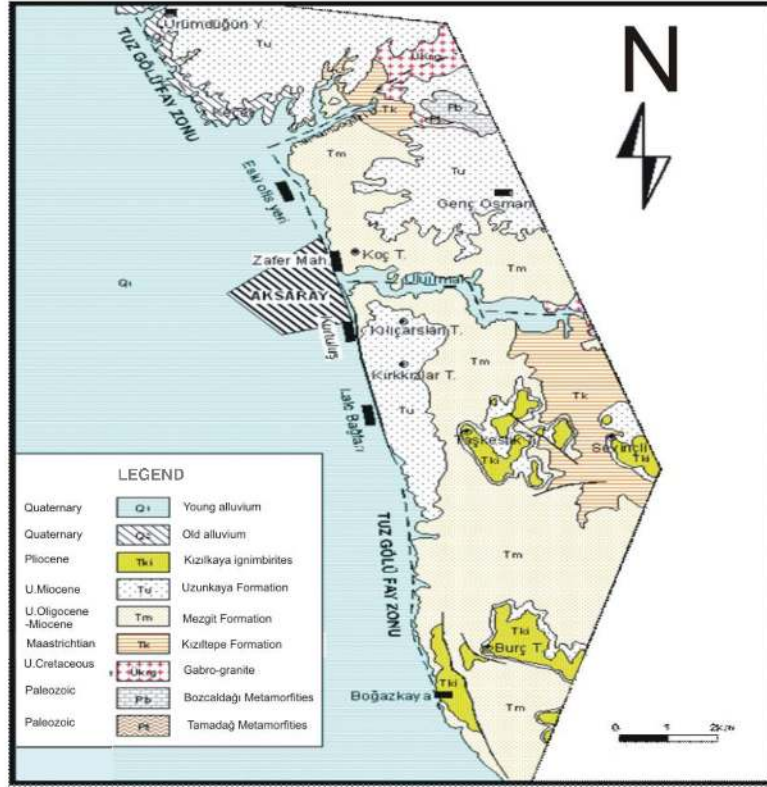


Fig. 2. Geologic map of the vicinity of Aksaray (Yıldız et al., 2002).

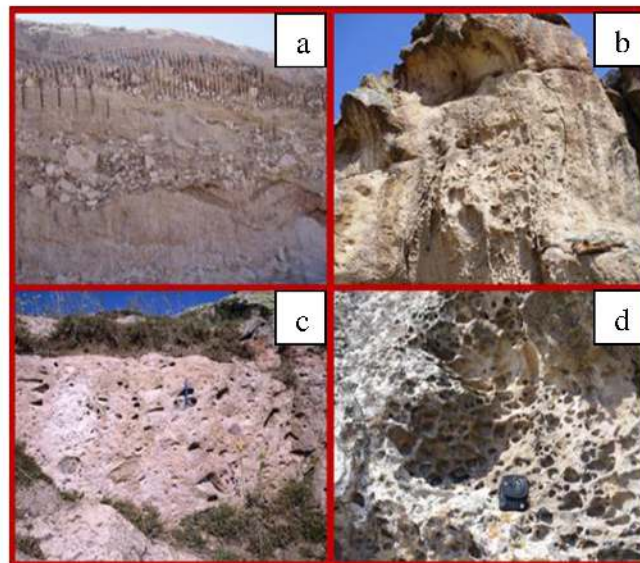


Fig. 3. General view of the Kızılkaya Ignimbrite

### 3. Material and Methods

Investigation material is ignimbrite from Sevinçli (Aksaray) area. Petrographic observations (optical microscopy) in thin sections of fresh samples were used to establish textural properties and to identify mineral species with Leica DM 2500 P polarizing in Aksaray University Geology Engineering Laboratory. Physical and mechanical tests on ignimbrite sample were performed in Afyon Kocatepe University, Department of Mining Engineering Laboratory. Data on the physical and mechanical properties obtained in experiment are given in Table 1. Interpretation of experiments given in Table 1 with related standards, besides these standards TS 10449 standards and TS 6234 have also been used.

### 4. Physical and Mechanical Properties of İgnimbrite

TS 2513 states that specific gravity could not be lower than  $2.55 \text{ g/cm}^3$  for natural building stones. Specific gravity of Sevinçli region ignimbrites is  $2.58 \text{ g/cm}^3$  and this value is close to standard as shown in Table 1. TS 2513 indicate that apparent density of natural building blocks should be of  $2300 \text{ kg/m}^3$  ( $2.30 \text{ g/cm}^3$ ). The apparent density of natural stone which used cover stone require up to  $2550 \text{ kg/m}^3$  ( $2.55 \text{ g/cm}^3$ ) according to TS 1910. Apparent density of Sevinçli ignimbrites is  $1.45 \text{ gr/cm}^3$  which is under the accepted value (Table 1). Maximum porosity value of natural stone to be used for cover stone is 2% according to TS 1910. Porosity value of study area ignimbrite is 25.5%, this value is very high according to the standard value. On the other hand 25.5% porosity value of ignimbrites in the study area offer possibility of evaluating the thermal insulation properties, since for thermal insulation, larger part of the rock pores should be closed pores. According this the study area ignimbrite has an ideal thermal insulation characteristic for buildings. Water absorption by mass should be lower than 0.75% according to TS 2513. The high water absorption value of Sevinçli ignimbrite indicates the high porosity of the rock. This porous structure of the rock is a disadvantage. Compressive strength of Sevinçli area ignimbrite has 9.81 MPa, as given in the Table 1. Uniaxial compressive strength of Sevinçli area ignimbrite show 'very low strength' value according to Deere and Miller (1966), also it is lower than value for metamorphic rocks (50 Mpa) given in TSE 2513. It can be concluded that high porosity of the rock decrease the uniaxial compressive strength to 9.11 MPa after freezing. Bending strength value of ignimbrite is 4.06 MPa. Bending strength value of natural building stone should be  $50 \text{ kgf/cm}^2$  (5 MPa) in TS 2513. Accordingly, bending strength value of Sevinçli ignimbrite is lower than given by TS. Ultra sound velocity of the Sevinçli ignimbrite has 2443 m/s, and the results are given in Table 1. The main reason is due to the high porosity. By increase the porous structure within the stone, the sound wave propagation and speed decreases. Schmidt hardness of the Sevinçli ignimbrite was obtained as 29.56 (Table 1). According to Schmidt hardness classification value the Sevinçli ignimbrite is a 'less rigid' rock (Brown, 1981).

Table 1. Standards used and results of the physical and mechanical properties of studied ignimbrite.

Test Name	Standart No	Result
Specific gravity ( $\text{gr/cm}^3$ )	TS EN 1936	$2.58 \pm 0.02$
Apparent density ( $\text{gr/cm}^3$ )	TS EN 1936	$1.45 \pm 0.17$
Water absorption (%)	TS EN 13755	$17.86 \pm 2.45$
Open porosity (%)	TS EN 1936	$25.5 \pm 0.86$
Compressive Strength (MPa)	TS EN 1926	$9.81 \pm 1.67$
Ultrasound (m/sn)	TS EN 14579	$2443 \pm 476.31$
Schmidt Hardness	ISRM	$29.56 \pm 3.94$
Bending Strenght (MPa)	TS EN 13161	$4.06 \pm 0.48$
Compressive Strength after freezing cycle (MPa)	TS EN 12371	$9.11 \pm 1.98$

### 5. Conclusion

Mechanical properties of studied ignimbrites were compared with TS 10449, TS 1910, TS 2513 and TS 6234. The results are listed below:

- Specific gravity of ignimbrites is suitable for interior and exterior works in flooring according to the TS 2513.

- Sevinçli ignimbrites does not provide the necessary requirements given in TS 10449, TS 1910, TS 2513, TS 6234 on compressive strength, compressive strength after freezing, bending strength, Schmidt hardness, porosity and water absorption. Therefore, Sevinçli (Aksaray) Kızılkaya region ignimbrites showing low strength in terms of physico-mechanical properties can be identified as more suitable for use in the interior works floors. In addition, because the high porosity value (25.5%) the ignimbrite in this region should be investigated in detail to determine their characteristics for the thermal conductivity.

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## SELECTED ELEMENT DISTRIBUTION IN BOTTOM SEDIMENT SAMPLES FROM TRÊS MARIAS LAKE AND ITS SIGNIFICANCE, MINAS GERAIS, BRAZIL

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**Abstract.** The Três Marias Lake is an important water reservoir at the upper to middle São Francisco River. It is important for irrigation, drinking water supply, fish raising and tourism. Therefore the water contamination is a very serious problem. The paper presents the connection between land uses/industry and water-/ sediment composition in space and evolution in time.

It is to observe that industry is not more the principal contributor and is replaced by intensive agriculture activity in the surroundings.

**Key words:** Water contamination, sediment contamination, agriculture, industry, environmental impact

### Introduction

South of the city of Três Marias a storage lake was installed and finished on 01.03.1963 to push the industrial and agricultural evolution in the São Francisco valley and to avoid future overflowing. The lake is situated in the municipal district of Andrequicè and touches the districts of Lassance, Buritizeiro, São Gonçalo do Abaeté, Morada Nova de Minas, Felixlândia, Corinto, affecting their hydrological situation and climate. The drainage area of the lake is about 50,600 km<sup>2</sup> and its surface is of about 1,090 km<sup>2</sup> with a volume of 19,528 hm<sup>3</sup>.

The investigated area is situated in the central-western part of Minas Gerais State, about 270 km away from Belo Horizonte, south of the city of Três Marias. The access is by BR-040 in direction of Brasília (Figure 1).

The climate of the region is subtropical to tropical with clear defined rainy and dry periods (Ab'Saber, 1971). The vegetation is a transition between Cerrado (Savannah), Dry Forrest and Caatinga (IEF, 2005). The lake shows distinct periods with high and low water levels (DNPM/MME, 1989), controlled by natural input, evaporation and dam regulation of the output. From the 80s the effective water reserve reduced to less than 40% in 2013.

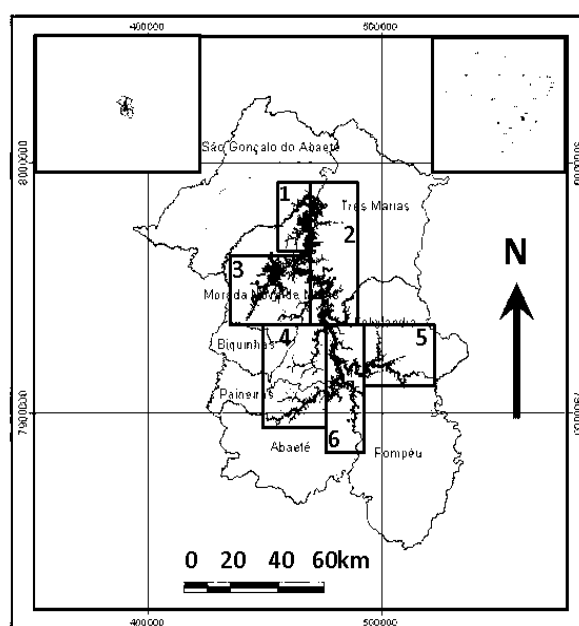


Figure 1. Localization map of the Três Marias Lake with the different sampling areas due to present contamination sources like river contribution, land use or other human influenced factors. (CPRM, 2003; modified).

1: **North-western Valley** – Family agriculture; 2: **Eastern Margin** – Traffic influence; 3: **Morada Nova Region** – Settling, fish raising; 4: **Extrema River** – Forrest economy; 5: **Paropeba River** – Heavy Industry, settling, forest economy; 6: **São Francisco Valley** – Extensive agriculture, forest economy.



The system of the lake including the drained area is intensively used by agriculture activities like cattle raising, seed production, forest exploitation for wood, charcoal and cellulose, extensive corn and cotton production and fish raising.

Almost the whole shores of the lake are influenced by extensive tourism, bathing, intensive fishing and boat traffic.

The nearby zones of the lake are influenced by heavy industry, agriculture, digging activities, sewage water and other contaminating sources (Figure 1).

The changes in land use around the Três Marias Lake are shown in Figure 2 (space images taken from different years).

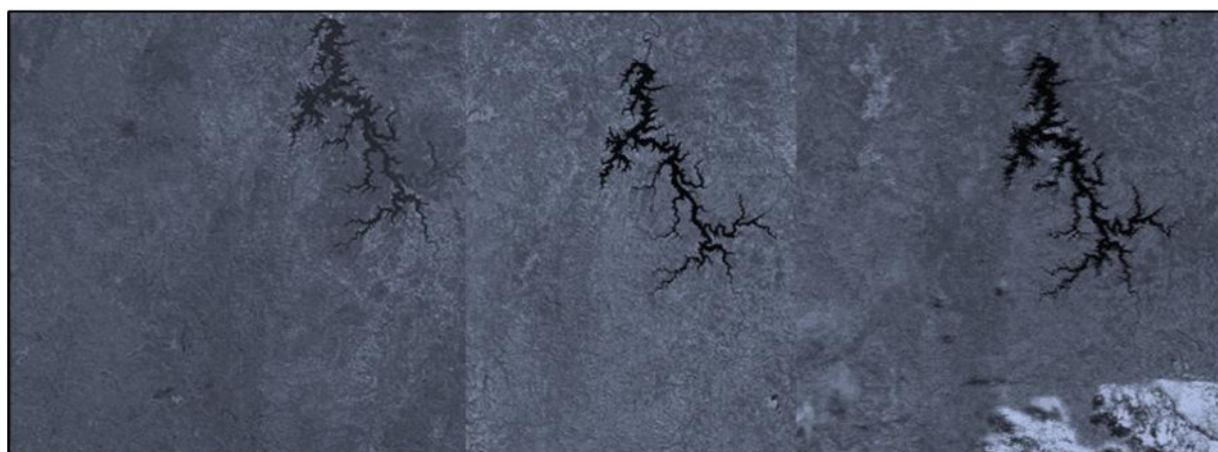


Figure 2. Space images showing the evolution of land use from 1990 up to 2010.

Left: Principally natural vegetation like savannah, dry forests and outcrops of sediments. Middle: Beginning of agriculture activities and forests; Right: Intensive forests) and agriculture activities.

### Activities

The method of field sampling and sample treatment was based on the guide by CETESB (CETESB, 1988).

### Field work

The sampling of sediments has been done by Schimith from 2011 to 2012 (Figure 1; eight campaigns) during six month and compared with data from Schilling (1991; one campaign) collected in 1990 and Oliveira (2007).

The localization has been done by triangulation (first campaign; 1990) and by GPS-localization (last campaigns; 2012). At the sampling points other physical-chemical parameters like temperature, pH, conductivity, eH, color, turbidity and DOB of the water were determined.

### Transport

The samples, water (1l), sediments (1-2kg), were transported to the laboratories in Belo Horizonte, sediment samples in plastic bags and bottles in cooling boxes. Then the samples were stored in freezers.

### Laboratory stage

#### Preparation of the sediment samples

The samples were dried, sieved and the fine fraction was analyzed.

The extraction was done by water (pH of rainwater), weak acid (10%  $\text{HNO}_3$ ) and concentrated acid (conc.  $\text{HNO}_3$ ).

### Analytics

For analyzing the selected elements the equipment of XRF (ACME-Lab) and ICP-OES (NGqA-IGC) was used with national and international standards.

### Results

The analytical results from sediment sample show that soluble metal concentration changes significantly from 1990 to 2012. The changes in concentration show the influence of increasing of environmental protection activities and the changes in intensity, quality and output of the principal sources (Table 1) together with the reduction of free metal ions in water samples and increase of clay- and oxide bounded ions.

Table 1. The average values of sediment data (all campaigns, 1, 2, 3, 4, 5, 6) in comparison with values and data from before (Schilling, 1991; Lundhamer, 1991; Horn & Sgarbi, 1993; 1a, 2a, 3b,4a, 5a, 6a). Areas can be seen on Figure 1.

	Pb mg/kg	Cd	Cr	Co	Cu	Ni	V g/kg	Zn	Sn	Al
1	85	1,5	234	9	160	39	110	45	8	9
1a	86	1,4	234	9	145	38	116	37	8	6
2	45	0,7	102	9	145	40	71	125	10	12
2a	53	0,8	96	8,5	130	37	70	130	10	8,9
3	125	7,5	850	33	195	12	240	85	35	16
3a	110	7	720	30	180	9	235	75	40	14
4	160	1,2	170	8	185	40	115	140	20	25
4a	158	1,2	168	7,1	53	43	120	157	19	20
5	70	0,4	150	7	38	40	110	140	18	20
5a	83	0,9	93	7	36	33	93	125	23	12
6	45	1,6	94	9,1	144	28	25	32	0	4,8
6a	0	1,4	69	8,8	124	25	20	25	0	3,7

Table 2. Indication of obtained water concentration for selected elements (all campaigns, 1, 2, 3, 4, 5, 6) in comparison data from previous works (Schilling, 1991; Lundhamer, 1991; Horn & Sgarbi, 1993; 1a, 2a, 3b,4a, 5a, 6a). Areas can be seen on Figure 1.

	pH	TCA	Zn	Cd	Al	Mn	Ni	As	K	Na
1	7,8	l	0	0	l	l	0	0	m	m
1a	5,3	m	0	0	0	l	0	0	m	nd
2	7,4	m	0	0	m	l	0	0	m	m
2a	5,4	m	0	0	m	l	0	0	m	m
3	8,1	h	l	l	h	m	l	l	m	m
3a	5,4	h	0	0	h	l	0	0	m	m
4	6,9	h	m	m	h	m	l	l	h	m
4a	5,4	h	0	0	h	0	0	0	m	m
5	6,9	h	m	l	m	m	l	l	m	h
5a	4,5	l	m	0	m	l	0	0	h	h
6	7,8	m	h	m	h	h	h	l	h	h
6a	5,8	h	0	0	m	l	0	0	0	m

Note: nd= not detected; l= low; m= medium; h= high concentrations.

### Interpretation

The comparison between the chemical data and other parameters of water and sediment samples shows that the values change. The principal distribution of contamination is changing from punctual to diffuse contamination (Table 2 and 3) and from Paraopeba to São Francisco River and the regions with agriculture utilization.

### Conclusions and discussion

Observing and interpreting the data from about twenty five years it can be concluded:

- The primary contamination caused by industries along the river reduces significantly;
- The change of the principal sources from the big industries to small and informal industries;
- The urban contamination increases from the past;
- The growing of agriculture, forest economy, fish raising in the Cerrado region is causing more and more diffuse metal and organic contamination of water, this is less visible in the sediments.

Sediment samples show the longtime contamination, indicating a reduction of the industrial participation from 1990 till 2010 in contaminant liberation.

The parallel taken water samples supported these considerations and indicate a stronger contribution of small industries, urban centers and agriculture activities (s.l.). The problem is the diffuse contamination caused by these activities reaching more parts of the river and complication processes of auto healing.

The temperature, conductivity, pH and turbidity distribution show the recuperation and force of the lake to recover or mitigate problems from the contributors to the dam.

### **Acknowledgement**

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**HEAVY METALS AND ALUMINUM CONTENT INSIDE SILICOPHYTOLITHS FROM  
RICINUS COMMUNIS, ANDROPOGON ARUNDINACEUS AND BRACHIARIA  
DECUMBENS GROWN ON SOILS ADDED WITH SEWAGE SLUDGE  
AND HEAVY METAL SALTS (BRAZIL)**

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**Abstract:** Silicophytoliths are opal corpuscles formed by some plants. These particles can trap small amounts of elements like Al and some undesirable heavy metals. In this paper elemental analysis of silicophytoliths of three species grown on soils added with sewage sludge and heavy metal salts were performed in order to verify amounts of heavy metals and Al they can trap. The results show that all studied plants can trap small amounts of heavy metals in their opal structure and that the plants that produce high amounts of silicophytoliths can clean soils fertilized with sewage sludge used in agriculture.

**Key words:** Phytoliths, sewage sludge, contaminated soils, phytoextraction, phytoremediation.

## **1. Introduction**

Phytoextraction (phythoremediation) has been suggested as a viable alternative to traditional restoration practices for heavy metal-contaminated soils in view of the lower costs and lower environmental impact (e.g. soil fertilized with sewage sludge and land fill areas of mines). The heavy metals and aluminum that plants extract are toxic, and the plants used for phytoextraction are known as hyper accumulators that have the ability to sequester large amounts of toxic metals both in their organic and mineralized parts (Oliva et al., 2011).

Mineralized tissues are common in animals and plants. In almost every phylum outside the animal kingdom taxa can be found in which biomineralization also occurs. Silicon is omnipresent in soils in the form of minerals and others, thus it is an element ubiquitous in the plant environment. Due to soil conditions silicon dioxide and aluminum silicates are normally only slightly soluble forming free silicic acid. The variations of Si-contents are low within a plant species. The Poaceae, generally have high silicon contents (>4% dry weight) while many other plant families are poor in silicon (Bauer et al., 2011).

Plants during their vegetative cycle absorb most of the Si as silicic acid  $[\text{Si}(\text{OH})_4]$  which, during transpiration and under polymerization process, is synthesized to opal silica (so called “plant-opal”,  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ). They form small (50-2  $\mu\text{m}$ ) opal corpuscles known as silicophytoliths which may also contain significant concentrations of other elements (Wilding & Drees, 1971). Silicophytoliths, besides Si and O, contain small amounts of Al, Fe, Mn, Mg, P, Cu, N and inorganic C ranging from 1% to 5% of total phytolith weight (Bartoli & Wilding, 1980). These elements are present in the cytoplasm of living cells and then retained when cells become impregnated with solid silica, becoming enclosed within the silicophytolith (Wilding et al., 1977). These particles have important beneficial physiological functions like the immobilization of plant toxic ions such as aluminum and heavy metals (Buján, 2013).

After senescence and decomposition of plant debris, the silicophytoliths are dispersed in the soil where they remain as one of their stable major components. Since the silicophytoliths have the ability to sequester heavy metals, and because they remain unchanged by weathering in the soil for many years, they can be used to recover contaminated soil with these elements through processes of phytoremediation.

The objective of this work is to find out which elements and in which quantity the selected plants can trap in their silicophytoliths. The plants were grown in soil with and without addition of sewage sludge

(*Ricinus comunis* and *Andropogon arundinaceus*, an hyper accumulator) and with and without addition of salts of heavy metals for *Brachiaria decumbens*.

## 2. Methodology

The experiments were conducted at greenhouses at the Institute of Agrarian Sciences of the UFMG localized at Montes Claros.

Two distinct test series were realized:

1. The used soil was an Inceptisol. Leaf samples of the *Poacea*, *Andropogon arundinaceus* and of the *Euphorbiaceae*, *Ricinus communis* grown on soil with and without addition of sewage sludge (dose: 30 t·ha<sup>-1</sup>; Table 1) were collected and submitted to phytolith separation using dry oxidation procedure as described by Parr et al. (2001).

**Table 1:** Important elements of the sewage sludge composition (trace elements determined by ICP-OES and ICP-MS analysis)

N	P	K	Na	Ca	Mg	S	Fe	Mn	Zn	Cu	Cd	Pb	Cr	Ni
----- % -----						----- ppm -----								
3,24	0,75	3,36	0,02	2,21	0,26	1,93	44,8	195,0	625,0	147,5	1,27	36,5	50,0	24,7

2. The used soil material was sampled from the 10 and 30 cm depth of a medium textured Oxisol (pH=4,8) with 20% clay. The neutralization of the soil acidity and fertilization was done according to the recommendations of Malavolta (1980) for greenhouse tests. The amounts of the heavy metal salts added (per kg of soil) were: BaCl<sub>2</sub> (0.2g); HgO (0.022g); Pb(CH<sub>3</sub>COO)<sub>2</sub> (0.04g); Zn (CH<sub>3</sub>COO)<sub>2</sub> ; MnO<sub>2</sub> (0.08g); Cu(CH<sub>3</sub>COO)<sub>2</sub> (0.2g); FeCl<sub>3</sub> (0,14g). The tests were done in 14 pots each with 5kg of soil. No heavy metal salts were added to the control pot and one pot was filled with a mixture of 50% sewage sludge and 50% soil material. In every pot three plants of *Brachiaria decumbens* were planted. The tests were done during the period of April to August with maintaining the soil humidity to 70% field capacity. The whole plants were cut, washed, dried; the silicophytoliths were extracted according to the wet oxidation procedure described by Parr et al. (2001).

The elemental analysis was performed by the ICP-MS ( Inductively Coupled Plasma Mass Spectrometry) Method.

## 3. Results

– The phytoliths of *Andropogon arundinaceus* (*Poacea*; MS e ed-XRF) show a significant presence of Si, de S, K, Ca, Cr e Fe (>10mg·kg<sup>-1</sup>). Zn and Cu were found in concentrations near detection limit and Al was not detected, fact that agrees with Carnelli et al. (2002) about the co-precipitation of Al and Si in annual grasses.

– The phytoliths from *Ricinus communis* show high Al, Fe, Ti and K contents (>500 mg·kg<sup>-1</sup>). Only slightly differences in element concentrations between the plants from pots with and without sewage sludge were observed. Table 2 shows the concentration of selected elements in plants grown on substrate with and without addition.

Table 3 shows the element concentration of *Brachiaria decumbens* plants grown on substrate enriched in selected elements as analyzed by ICP-MS and ICP-OES.

## 4. Discussion

The obtained results show that all plants can trap elements in their biogenic opal structures. There is probably a competition between Si and Al inclusion which vary from species to species.

In substrates containing sewage sludge, there is lower concentration of heavy metals in the plant phytoliths, possibly due to strong bonds with organic matter and hence low element absorption. Another possibility is for heavy elements concentration in roots silicophytoliths, not analysed yet.

**Table 2:** Concentration of elements in phytoliths from *Andropogon arundinaceus* grown on substrate with or without sewage sludge addition. The analyses were done with ICP-MS equipment. The results show significant enrichment of some interest trace elements in the leaves.

Factor	Fe	Mn	P	K	Ca	Mg	Al	Ti	Mo	Cd	Cu	Ni
	%								ppm			
Without sludge	0,03	11,00	0,04	0,08	0,08	0,04	0,08	<0,01	17,56	0,05	28,91	3,10
With sludge	0,03	8	0,08	0,04	0,02	0,01	0,19	0,04	8,3	0,41	118,8	2,9

Factor	Pb	Zn	Cr	Ba	B	Sc	Ga	Hg	Ag	Re	Pt
	ppm								ppb		
Without sludge	499,1	11,6	1,9	12,0	<20	0,2	0,1	0,1	105	<1	<2
With sludge	88,24	2,5	4,9	16,5	80	0,5	2,0	0,3	418	2	<2

**Table 3:** Element concentration in phytoliths of *Brachiaria* grown on contaminated substrates. The analyses were done by ICP-MS. For comparison some data from geological opal formed in volcanic environment with high element concentrations in the solutions (Marinoni et al., 2012).

Factor	Fe (%)	Mn (ppm)	Cu (ppm)	Zn (ppm)	Ba (ppm)	Hg (ppb)
Soil with Fe	0,05	9	35	11,33	13	0,1
Soil with Mn	0,04	12	33	12,1	14	0,1
Soil with Zn	0,03	8	29	2,9	12	0,2
Soil with Cu	0,02	10	453,2	12,5	12	0,1
Soil with Ba	0,03	10	28	11,8	25,8	0,2
Soil with Hg	0,03	10	28	11,3	11	0,5
Soil/Sewage sludge	0,03	8	118,8	2,5	16,5	0,3
Pure soil	0,03	11	28,91	11,6	12	0,1
Volcanic opal	0,02-0,05	42-45	3-15	2-6	4-5	-

However, for Ba and Cu there is a significant increase in their concentration when the *Brachiaria* plants grown on soil that contains high concentration of these elements; this is in agreement with results obtained by Oliva et al. (2011). In soils that received sewage sludge (source of Cu) it was noted a great increase of concentration in this element in the silicophytoliths. This fact shows the phytoliths importance in sewage sludge phytoremediation for agricultural use.

The processes of incorporation and the regulating factor are still not very clear and need more studies. Still the fact that plants retain considerable amounts of elements in their silicophytoliths and that this particles liberate slowly the trapped elements than the biological part of plants can be used in decontamination processes and impact mitigation. But how the plants retain elements in their silicophytoliths and they are less soluble than plant parts they can be used in decontamination processes and/or impact mitigation.

The results of this investigation may help to plan phytoremediation actions in order to decontaminate areas by the selection of plants that are able to incorporate heavy metal contaminants inside their silicophytoliths.

## 5. Acknowledgement:

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## **RAINFALLS AND NATURAL DISASTERS: THE 2011 - 2012 EVENTS IN MINAS GERAIS STATE - BRAZIL**

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**Abstract:** This brief communication was compiled from recent data on the latest events of natural disasters 2011/2012 in Minas Gerais State. In Brazil, the risk associated with accidents and geological processes are purely exogenous, with landslides and related processes which cause much loss of life. These natural phenomena are often conditioned by atmospheric general circulation systems operating in the region of Brazil, especially during summer, and use geological and other variables in the following order: geomorphological, topographical, pedological, hydrological and land use. The summer of 2011/2012 began catastrophically; it was characterized by one of Brazil's worst ever natural disaster, the scene of the tragedy was the Minas Gerais state, namely several municipalities in Minas Gerais. According to the State Civil Defense, the tragedy implied 2,495 people, the number of homeless rose to 25,514 and 15 people have died and 3 were missing.

**Keywords:** Minas Gerais, rainfall, natural disasters, tragedy

### **Introduction**

Natural disasters are a theme more and more present in everyday's people lives, independently whether they live or not in areas of risk. Although at first sight the term leads us to associate it with earthquakes, tsunamis, volcanic eruptions, cyclones and hurricanes, Natural Disasters also include processes and more localized phenomena such as landslides, flooding, subsidence and erosion, which may occur naturally or induced by man. Brazil is among the most affected countries by floods and disasters of the world, having recorded 94 registers in the period from 1960 to 2008, with 5,720 deaths and more than 15 million people affected (homeless/displaced); the most natural disasters are associated with severe weather events that are responsible for triggering floods, windstorms, hail and landslides. Over 60% of these events occur in the south-southeast part; in those regions atmospheric instability is common due to cold fronts in the winter, occurrences of mesoscale convective complexes in the spring (MCC) and the formation of convective systems in the summer, especially The South Atlantic Convergence Zone, or SACZ, these systems achieve a wide range of central Brazil (Instituto Geológico, 2009). The summer of 2011/2012 began catastrophically, it was characterized by one of Brazil's worst ever natural disaster, the scene of the tragedy was Minas Gerais State, where several municipalities - 62% - were affected by disasters related to severe rainfall events. In the first seven days of January 2012, it rained in Belo Horizonte corresponding to 22% above the expected average for all the month, 334 mm of rain, causing flooding in various parts of urban areas, floods and gravitational mass movements - landslides. The total number of homeless and displaced people in Minas Gerais due to floods that hit several cities doubled after the update data made by the State Civil Defense – CEDEC/MG, and exceeds 2,495 people, the number of homeless rose to 25,514 and 15 people have died and 3 were missing (CEDEC-MG, 2011).

### **Location and physiographic features**

Minas Gerais is one of 27 states of Brazil, located in southeastern part being the fourth largest in area – 586,528 km<sup>2</sup> - the state is the second most populated in Brazil, with almost 20 million habitants. The state capital is Belo Horizonte, with about 5,5 millions habitants, and thus, the third largest urban agglomeration in the country. The state of Minas Gerais is located between parallels 14°13'58" and 22°54'00" South latitude and meridians 39°51'32" and 51°02'35" W-Gr. Altimetrically the altitude ranges from 450 to 1,700 meters. The relief of Minas Gerais includes 5 relief units: Crystalline plateaus, Espinhaço Range, San Franciscana depression, São Francisco Plateau, and Paraná Plateau, resulting from an alternation of processes: morphoclimatic, morphostructural, morphosculptural and morphotectonic (CEDEC, 1983).

Reis (2001) defined the climate for Minas Gerais as follows: Aw - Tropical rain; Cwa - hot tempered; Cwb - cold tempered. Average annual rainfall in Minas Gerais varies from 900mm to 1,800mm. Temperatures vary from 23°C to 24°C. Rainfalls during the summer months are intensified, causing floods and landslides in several municipalities of the state, due to the occurrence of the Convergence Zone of the South Atlantic (SACZ). The SACZ is usually oriented northwest-southeastward and is

associated with a convergence zone in the lower troposphere, which extends from the south of the Amazon to the Atlantic Center, a few thousand kilometers (Diaz, 1992). Originally the vegetal coverage of Minas Gerais is made up of four major biomes: Cerrado, Atlantic forest, Dry forest and Rupestris fields (CETEC, 1983).

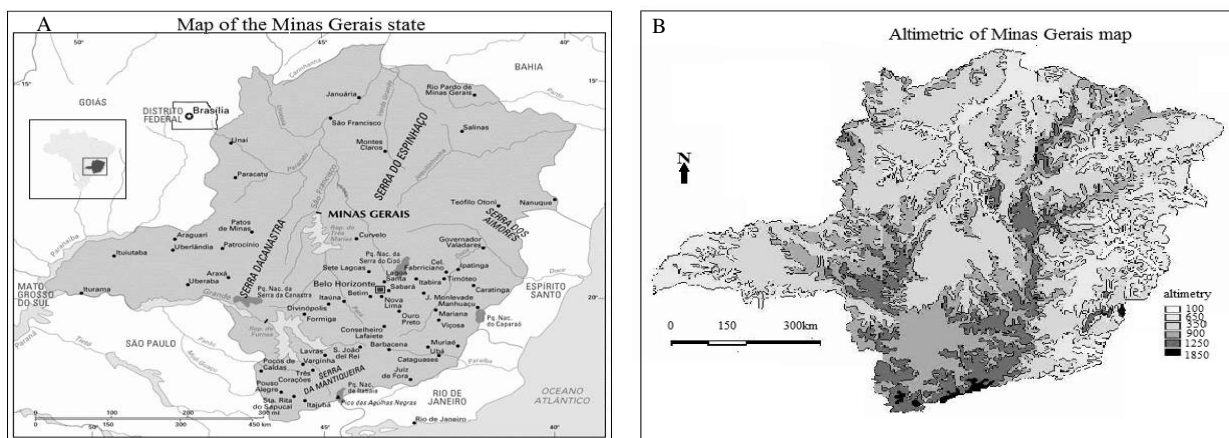


Fig. 1. (a) Location map of Minas Gerais and (b) altimetric map. Source: CETEC-MG, (1983).

## Methods

For this compilation of recent data on the latest events of natural disasters 2011/2012 in Minas Gerais State, the work had a qualitative character. Some activities are considered of paramount importance in planning the project methodology, among them: bibliographic and cartographic research, which consisted in a comprehensive survey and review of surveys as well as studies in risk areas, environments and also aspects of the physical, economical, social and environmental context of regional and local area surveyed. All data were tabulated and maps have been generated using Corel Draw X3 software.

**Results and discussion:** Irregular occupation of risk areas without soil use planning, associated to climate changes, have caused disasters in the world, with such intensity that forces us to reflect on the occupation of the planet and the need of changing attitude. In the last rainy season, Brazilian media showed several disasters. Among them, we highlight the floods and landslides that occurred in the mountainous region of the State of Rio de Janeiro, where there were recorded 919 deaths, 4,563 injured and 252,680 people affected. It shows that the result of the disaster magnitude presents significant numbers of human damage, without considering the environmental, economic and social damage. In the State of Minas Gerais, 25,32% of the cities were hit by rain-related disasters in the period 2010/2011 and 2012, the south and the Zona da Mata together accounted for 40,05% of total disaster and were the most affected (CEDEC-MG, 2011).

## Evolution of rain-related disasters in the State of Minas Gerais

During the last rainy season (2010/2011), an increase of 0,47% in the number of municipalities affected by disasters caused by heavy rains in Minas Gerais State has been noticed, compared to the historic average of the last nine years, which was of 216 municipalities in this period (Fig. 2). Regarding the number of processes homologated, there is an increase of 12,79% compared to the historical average of 86 cases (Table 1).

Figure 3 shows that in the period 2009/2010, the highest incidence of rain-related disasters occurred in November and December, the largest volume of rainfall recorded. During this period (2010/2011), the highest incidence was in January, which recorded 38.43% of the municipalities affected, followed by the month of December with 24.07%. It was registered during the two months together 62.5% of total disasters. Through the evaluation form of damage (Avadan) the human damage, environmental and economic and social losses of the municipalities affected by rains were measured in the period 2010/2011. The losses were in the order of US\$ 515,635.198. In comparison with the average of the three previous periods (2007-2010) US\$ 196,612.161, there was an increase of 162,26% in the total measured by Avadan (CEDEC-MG, 2011).

Table 1. Number of municipalities affected by the disasters caused by heavy rains in the State of Minas Gerais in the period 2001 to 2011.

Disaster	2001/02	2002/03	2003/04	2004/05	2005/06	2006/07	2007/08	2008/09	2009/10	2010/11
Municipalities affected	239	261	218	234	152	316	121	276	210	216
Processes homologated	169	136	105	50	20	158	7	100	29	97

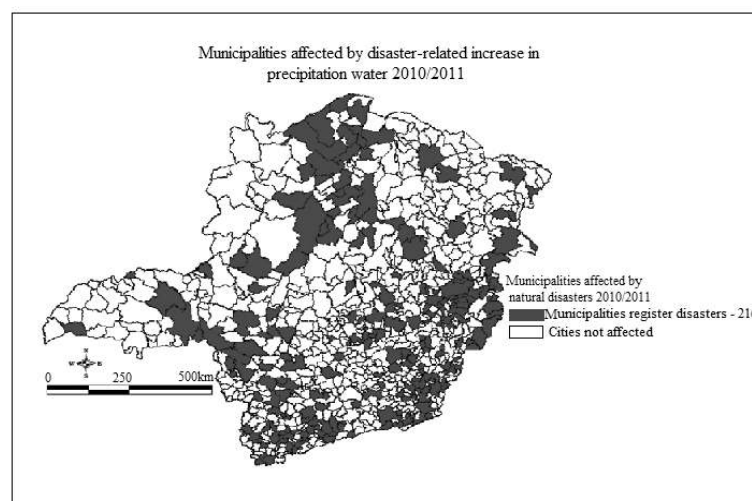


Fig. 2. Cities most affected by natural disasters (floods, flooding and landslides). Source: CEDEC-MG, (2011).

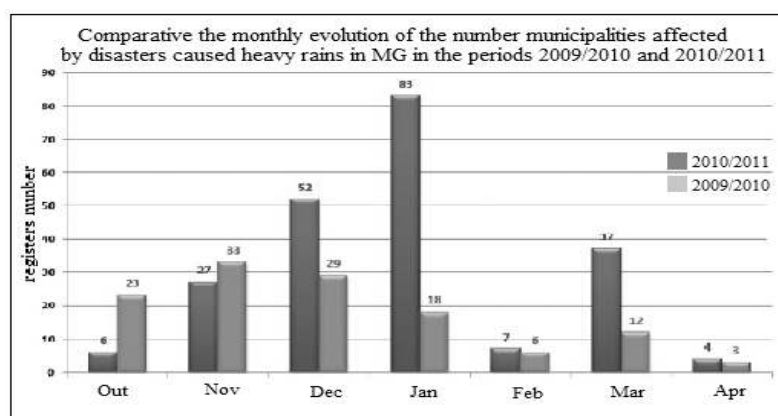


Fig. 3. Comparison of the monthly evolution of the number of municipalities affected by disasters caused by heavy rains in Minas Gerais in the periods 2009/2010 and 2010/2011. Source: CEDEC-MG (2011), modified by Baggio (2012).

### Consequences of natural disasters

During the weeks of the disaster Minas Gerais was under the influence of the convective system called The South Atlantic Convergence Zone - SACZ, characterized by a intense channel of moisture which extends from the North region to the Southeast region ( Figure 4). According to the National Institute of Meteorology, INMET, on the first seven days of January 2012, it rained in Belo Horizonte the total of 22% above the average previewed for the month. According to the Meteorological Institute of the Energy Company of Minas Gerais – CEMIG, it rained 334mm when the expected was 274mm for the whole month.

### Conclusions

Every year history repeats itself, when summer comes and with it the rainy season, there comes the suffering of the underprivileged class, who normally lives in risk areas, the hillsides that surround the major cities in the Southeast. Natural disasters in Brazil and in Minas Gerais state are a foretold tragedy:

authorities fail to provide safe housing outside risk areas for low-income populations, therefore they occupy risk areas. The disaster is announced by geoscientists, it is just a matter of time. The municipal and state authorities are fully aware of the fact. Hundreds of lives were and will be lost, physical structures were and will be destroyed, in addition to a large amount of biological and animals losses. The occupation of risk areas should be strictly forbidden; however, most families are not able to afford adequate housing and occupy the hillsides. How long will the country witness this kind of tragedy? Actions must be taken immediately, before the next summer, to prevent the repetition of these tragic incidents.

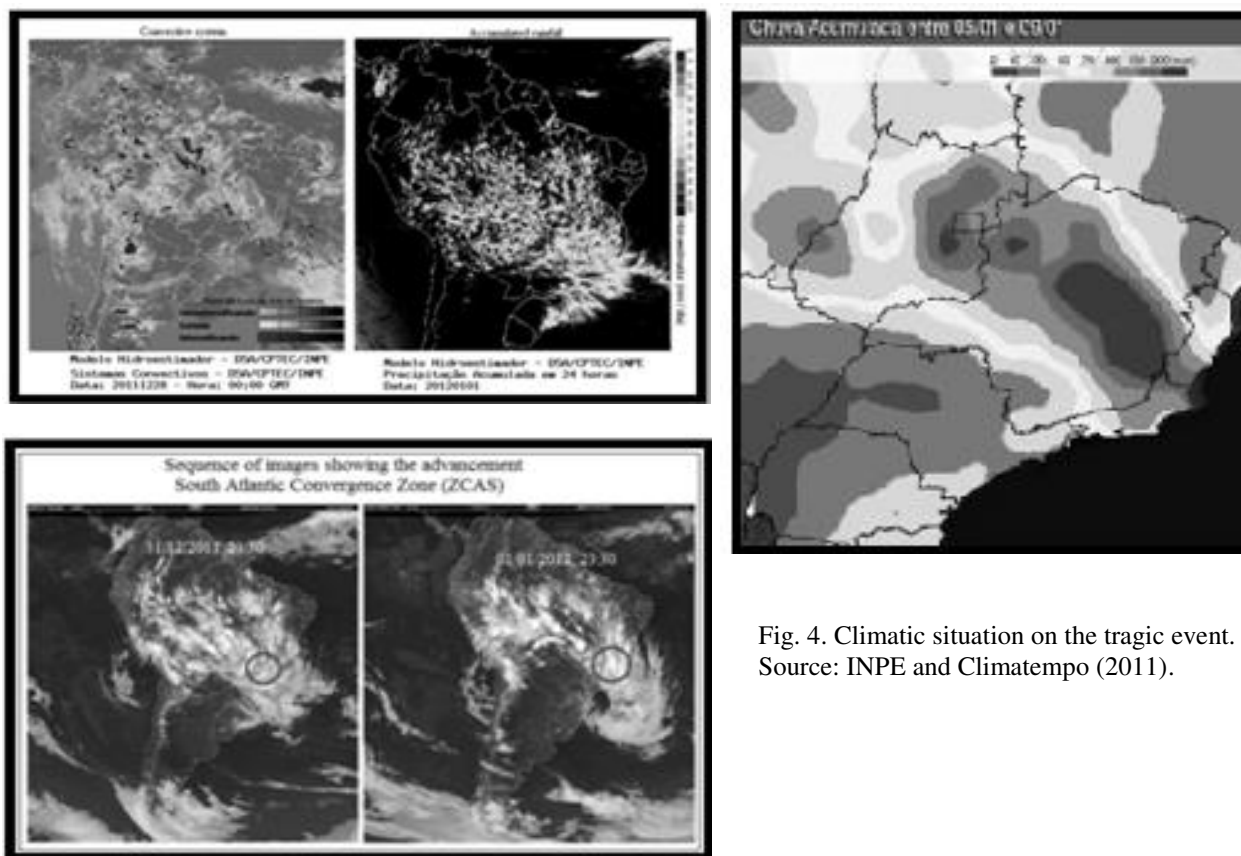


Fig. 4. Climatic situation on the tragic event.  
Source: INPE and Climatempo (2011).

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## INCIDENCE OF SEWAGE SLUDGE FERTILIZER APPLICATION ON RAY GRASS (MOROCCO)

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**Abstract:** The land application of sewage sludge reveals a significant increase in the dry matter production of Ray Grass. In equivalent dose of liquid mud, we registered a lower production of dry material, which could be the result of a loss though lixiviation of a quantity of nitrogen brought by mud. Besides, neither the dose nor the type of mud seems to have an effect on the Pb, Cd, Cu and Zn contents in the air part of the plant. On the other hand, it noticed that the contribution of mud under dry or liquid forms increases significantly the contents of Cd, Pb and of Zn in roots with regard to the witness without mud.

The comparison between the beginning and the end of culture, revealed a decrease of the content in Cd, Zn, Pb and Cu in the ground in particular at the level of the superficial coats (0-40 cm). Besides, this decrease of the contents in Cd, Zn, Pb and Cu in the ground is in no case connected to increase in the air part of the plant but rather, is for an accumulation in the roots, which play the role of a barrier, or a migration of these elements beyond roots.

**Key words:** the residual sludge, heavy metals, transfer, soil.

### Introduction

The contamination of grounds by elements in tracks is a major environmental problem for two reasons. Firstly, it presents an ecotoxicology risk for food chains because of the strongly toxic properties of these elements for all the human beings. Secondly, this contamination can have very long-term effects because elements in tracks present generally a strong chemical and physical affinity for the solid matrix of grounds and have a residence time in grounds very long (Echevarria and More, 2006). The assessment of risks associated to the soil pollution requires, not only knowledge of the total content in metal, but also the content in metal in the various constituent compartments of the ground (Jeans, 2007).

The heavy metal (Cd, Cr, Cu, Hg, Ni, Pb, Zn, etc.) are unwanted constituents of the urban sewage sludge. As some of them are potentially toxic and present no agronomic interest, their presence generate a certain concern, perfectly understandable when it is about spread this waste on grounds intended to produce food for the Man or the animals.

The agricultural use of the residual mud allows the recycling of precious components such as the organic matter and many nourishing elements of the plant (Logan and Harrison, 1995). It aims at arranging natural resources and at avoiding any wasting of organic matter due to the incineration or to the burying in the discharges (Lambkin and al, 2004); residual muds can replace or reduce the use of expensive fertilizers.

### Materials and methods

The ground of the try is argil - sandy in sandy-clayey, it is characterized that by an alkaline pH (7,50 - 8,31), an electric conductivity from 0,42 to 0,89 ms / cm what indicates a low of salinity bound to the sandy nature of the ground and a low content in total limestone (5 %) and in organic matter (0,39 % a 1,98 %). Besides, we note a better composition in organic matter, N and P in the superficial coat (0-20 cm) compared with the other horizons (20-40) and (40-60) (Table 1).

Used muds are native of the water-treatment plant of Korba. Mud stemming from this station have sudden a stabilization in aerobe followed by a drying on beds. The analysis of both chaps of muds (liquid and dry) shows that they are very different by their chemical compositions. The pH is acid and their electric conductivities translate an important salinity. The Fe and Zn contents are the most represented. The average contents found in dry muds is organizing to the following sequence: Fe >> Mn > Zn > Cu > Pb > Ni > Cd > Co. The average contents of heavy metals brought by muds are representing on the Table 2.

The plant material used in our experiment is the English Ray Grass (*Lolium perenne*). In this study, we made five successive cuttings at 3 cm of the surface of the ground, at the interval of month. Five treatments retained for this experiment.

Besides the treatment Witness, four treatments including two types a dries mud and a liquid mud (thickened mud) brought each there two doses (5 and 10t / ha) were applied in four repetitions: Treatment T: Witness without contributions of muds control; treatment 5 BS: contribution of dry muds 5 t/ha the equivalent of 0.5kg / m<sup>2</sup>; treatment 10 BS: contribution of dry muds 10 t / ha the equivalent of 1kg / m<sup>2</sup>; treatment 10 BL: contribution of liquid muds 10 t / ha the equivalent of 1 l/m<sup>2</sup> and treatment 5 BL: contribution of liquid muds 5 t / ha the equivalent of 0.5 l/m<sup>2</sup>.

Table 1: Physico-chemical Characteristics of the various horizons of the ground

Parameters	0-20 cm	20-40 cm	40-60 cm
pH	8.03	8.18	8.06
CE (ms/cm)	0.61	0.58	0.70
MO (%)	1.58	1.07	0.65
Total limestone (%)	1.12	2.12	2.28
N (%)	0.05	0.04	0.03
<b>Heavy metals (ppm)</b>			
Mn	136.50	125.00	107.40
Pb	34.40	29.80	28.40
Cd	2.06	1.72	1.23
Co	3.47	3.72	2.77
Cu	10.25	8.75	4.00
Fe	5337.00	7000.00	4638.00
Zn	22.50	21.70	17.90
Ni	14.07	13.10	11.20

Table 2: Physico-chemical characteristic of the sewage sludge

Parameters	dry mud	liquid mud
pH	6.46	6.30
Humidity (%)	33.30	95.40
CE (ms/cm)	6.95	6.17
MO (%MS)	40.20	94.00
N (%MS)	3.35	5.80
C/N	8.56	7.94
<b>Heavy metals (mg/kg of dries matter)</b>		
Mn	349	108
Pb	135	393
Cd	22	28
Cu	206	413
Fer	6954	9456
Zn	331	848
Ni	30.1	347

## Results

The result indicates an increase of the dry material according to the brought dose (fig 1). However, for liquid muds, the contribution of 5t/ha had no significant effect on the production of dry material, while the dose 10t/ha is accompanied by a significant increase of the production of the dry material compared with the Witness without contribution of mud. This increase of the production of material dry registered with treatments muds is probably the result of the contribution by muds of essential nourishing elements for the growth of the plant, such as the nitrogen and the phosphor.

For the same applied dose, the production of dry material is more raising if dry mud was applied. With liquid muds, a loss by lixiviation of a quantity of nitrogen brought by muds is probable. The comparison between both types of mud shows that the contribution of 10t/BL is equivalent to the contribution of 5t/BS from point of view effect on the production of dry material. The contribution of liquid mud has no positive effect on the production of roots (Table 3). However, a significant increase of the weight of roots registered with dry muds. We also note a significant effect of the dose of mud dry on the dry roots. It expressed by the concentration of diverse metals measured in the air parts of the Ray Grass. We note absence of effect measures of mud on the content in Zn of the plant. Besides, the

comparison enters cutting show a significant increase of the content in Zn obtained with cuttings four and five as well for the dry mud as the liquid mud.

This increase is linking to a competition between Zn and Cd. With liquid muds, no effect of the dose of mud on the content in Cd of the air part of the Ray Grass. For dry muds, the contents tend to increase with the contribution of muds in the dose of 10 t/ha for the first three cuttings. The air part of the Ray Grass is not effect of the dose or the type of mud on the content in Cu. The average contents in Pb oscillate around 8 ppm. These values are situating below threshold of toxicity of vegetables (30 ppm). We not registered effect about liquid. The sampling of roots are realizing further to the last cutting of the ray fat. Their composition in heavy metals is representing below (Table 4).

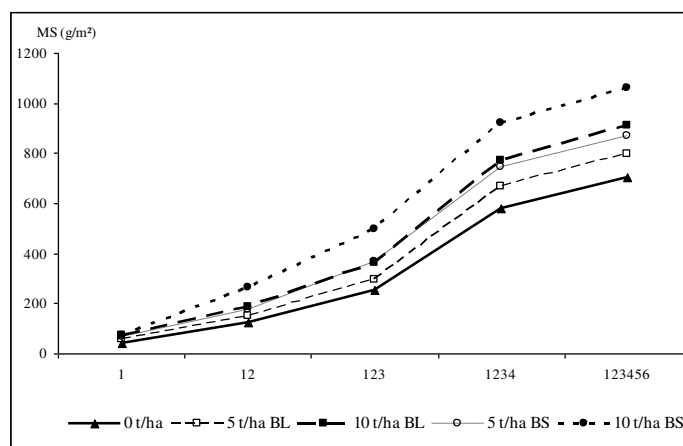


Figure 1: evolution of the production accumulated by material dry of the air part according to the various doses of liquid mud and dry mud.

Table 3: Effect of liquid and dry muds on the production of root

	Witness	5t/h BL	10 t/h BL	5t/h BS	10 t/h BS
<b>Zn</b>	68,6	101,4	113,1	99,6	103,7
<b>Pb</b>	13,9	14,1	15,7	15,9	17,5
<b>Cu</b>	19,8	22,6	24,3	25,7	25,7
<b>Cd</b>	1,3	2,1	2,5	2,1	2,7

Table 4: contents of elements metallic tracks Pb, Cd, Cu and Zn at the level of roots cultivated their presence of increasing doses of liquid and dry residual mud.

Treatments	Control	5t/h BL	10 t/h BS	5t/h BS	10 t/h BL
MS (g/m <sup>2</sup> )	19 680	24 000	51 540	33 700	32 120

According to Table 4, one can notice that the contribution of muds increases significantly the content in Zn, Cd and Pb in roots compared with the witness without any contribution. However, for the Pb and the Cd a significant effect of the dose indicated in roots as well for liquid muds as for dry muds. For the Cu, no effect was noted.

The analysis of the ground realized after the last cutting of the ray grass, shows a significant decrease of the content of the Zn in the superficial coat of the ground (0-20 cm) for both doses and both types of brought muds. As for the deeper coats (20-40 and 40-60 cm), no significant effect of the dose of dry mud was noticed on the content of Zn in the ground between the beginning of the try and after the last cutting. However, for the liquid mud in particular for the dose 10t / ha the content of Zn tends to decrease between the beginning and the end of the try. For the Pb, we note a significant decrease of the content in Pb of the ground between the beginning and the end of the try in the superficial coats. This decrease is also observing in the deeper coats of the ground (20-40 and 40-60 cm). Besides, for the Cu, the contents flopped between the beginning and the end of the try in coats 0-20 cm and 20-40 cm. On the other hand, those contents did not change in the coat 40-60 cm.

At the end of the culture, the Cd contents decrease significantly in the superficial coat (0-20cm).The contribution of both types of mud and the brought dose show the same evolution of Cd. With



the contribution of dry muds, the contents of Cd increase in the coats of the ground (20-40 and 40-60) at the end by the culture, we can say that the Cd migrated in the ground. The same effect is with the contribution of 10 t/ha of liquid mud.

The water leaving the lysimeter boxes for the different treatments is analyzing in order to explore the possibility of migration of heavy metals to the water. The analysis of drainage water showed for various mud treatments (Table 4) that the levels are not significantly different of control treatment. This suggests that the Cd, Zn, Cu and Pb retained rather in the soil.

### Discussion and conclusion

The spreading of liquid and dry muds resulted in an increase in the production of biomass Ray Grass. This increase is a function of increasing doses applied. This positive effect of muds on yield was found in other cultures. Indeed, many authors (Rejeb et Bahri, 1995; Rejeb et al, 2003) reported a significant increase in yields of various crops such as sorghum, corn, chili, potato. Our tests also showed a better performance with dry mud slurry with the year of application. This could also be the result of a share of a probable loss of nitrate made in slurries and other wealth of the mud brought dry matter. Indeed, the content of the sludge dry matter varies about 5% and 67% dry matter, respectively, in the slurry and dried mud.

Moreover, the contribution of muds caused an enrichment of soil by heavy metals and more particularly to the surface horizon (0-20cm). But this increase is not significant except for Cd. The content of this element has indeed increased, significantly in the presence of muds. In the lower ground (20-40 and 40-60 cm), levels of Pb, Zn, and Cu remained equivalent to the witness.

Regarding the accumulation of heavy metals in the plant, our results showed that the contents of Cd, Pb, Zn, and Cu in the aerial part of the plant does not vary with the addition of 5 and 10 t / ha of dry or liquid mud. These results are in agreement with those of Berthet et al. (1983) who studied the evolution of the levels of Pb in tissues of ray grass, subject to three types of treatment (control without, mineral fertilizer and sludge amendment). The flow trace metals made by urban sludge are very low on the scale of a year and their accumulation does not represent a risk to the environment if the prescribed conditions are met (Maisonnave et al, 2003). However, the accumulation of trace metals depends on the plant species. In addition, the response of plants to metals in sludge also varies depending on the elements.

In this work, analysis of drainage showed that the addition of increasing doses (5t/ha and 10t/ha) liquid and dry sludge has no significant effect on the levels of Zn, Cd, Plumb and Cu in lixivium; these levels are negligible and similar to the witness.

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## **PREDISPOSING FACTORS FOR SHALLOW LANDSLIDES SUSCEPTIBILITY IN SOUTHEASTERN RIO DE JANEIRO, BRAZIL**

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**Abstract:** Applied structural geology and geomorphological characterization studies were carried out, aiming an environmental analysis, with the assistance of field surveys, fusion images from thematic maps. The choice of this area in the Rio de Janeiro State - Brazil, was motivated by the recent rising of records of the dangerous landslides in that region, triggered by heavy summer rainfalls. Morphometric characteristics of features, such as shape, slope and aspect were analyzed. After the cartographic work of these features with the aid of Geographic Information System (GIS) technics, using superimposed layers of information and map algebra, charts were build, where the critic areas were highlighted, with the purpose of subsidize environmental studies. The SE area of Rio de Janeiro brings together factors that made possible the high susceptibility of landslides; these factors can be natural or anthropogenic. However, this paper intends to focus on the disposition of the predisposing agents that came from the heterogeneities linked with physical environment characteristics, such as mechanical discontinuities (in soil/rock structures), weathering and geomorphology parameters (shape, slope, aspect).

**Keywords:** Environmental Geology, Applied Structural Geology, Landslides, Rio de Janeiro-Brazil.

### **1. Introduction**

In the Rio de Janeiro State, SE-Brazil, landslides are the major environmental problem. These landslides (herein referred as LSD) are characterized as having many dimensions and the most common type is a shallow planar, mobilizing thin soil above weathered granite/gneisses rocks in medium to high grade hill slopes. They are spatially controlled by geology and geomorphology factors, among others. Heavy rainstorms in summer are the main landslide triggering factors. The use of Geographic Information System (GIS) and morphometric data of hydrographic basins helps the understanding of these processes origins and its statistical connection with geological discontinuities of the study area. This research has the goal to comprehend which kinds of natural geologic elements are associated to this phenomenon. The GIS tools were used to make this study and to elaborate topographical survey, hypsometric, slope and structural-geologic maps.

The results indicate that these gravitational mass movements are closely related with the existence of major heterogeneities, like shear zones roughly trending NE, brittle faults, foliations, fractures and joints, which promote the action of the water inside the mass, increasing the susceptibility of slopes to failures. Medium to steep slopes associated to the morphological characteristics of those hills facing NW, near the same orientation of regional foliation dips, have the better potential to failure. The combination of those data is useful to understand these mechanisms and to avoid natural hazards. So they tend to be more common in the NE trend, facing NW, in the study area, SE-Rio de Janeiro, Brazil. Pre-Cambrian basement is part of the Central Mantiqueira Province, Brazil, and their structures are related to the Neoproterozoic Brasiliano/Pan African Cycle (Hasui & Oliveira, 1984).

The catastrophic event of January 2011 in the Serrana Region of Rio de Janeiro is considered among the worst natural hazard in Brazil's history. Heavy rainfalls in that mountainous area led to the deaths of more than 900 inhabitants, and affecting more than 300,000 people. LSD triggered due to extreme rainfall was the major problem. According to the World Bank, it is estimated that the damage amounted to a total cost to be of R\$ 4.78 billion. Social sectors suffered the most damage, with a total cost estimated of R\$ 2.69 billion. The costs of containment slopes were budgeted at about R\$ 1.3 billion. In the Water/Sanitation sector, the cost of repair or reconstruction of canals and drainage systems represents approximately 89% of the total. Finally, the productive trade sector was the second most affected one, with total costs estimated at around R\$ 469 million (Toro et al., 2012).

## 2. The Investigated Area

The investigated area comprises a coastal area of the Southeastern of Brazil that has a very complex geology and topography, which reflects the neotectonic activities affecting this portion of the Precambrian chain during the Neogene-Quaternary (Cogné et al. 2012). It suffered the influence of the evolution of the Rift/Passive Margin (Jurassic/Cretaceous Gondwana breakup) and had the influence of Cretaceous Hot Spot (Sadowski & Dias Neto, 1981). During Paleogene, continental rift was formed in SE-Brazil (Riccomini et al., 2004). The rift is roughly parallel to Brazil's coastline and, in the study area, occurs one of its segment, the Guanabara Graben. Along this coast, the rift elongation is clearly influenced by the weakness of the pre-existing Precambrian structures, a NE trending Mega-Shear Belt, the Atlantic Shear Belt (Machado & Endo, 1993) with a transpressive Positive Flower structure. These zones are steeply dipping to NW, SW or vertical. The Serra do Mar ranges has a great escarpment and dominates the high topography of SE-Brazil coast.

Two distinct Precambrian tectonic domains are recognized in the study area: Litoral Fluminense Domain and Paraíba do Sul Domain. These domains are separated by a Ductile Shear Zone (DCZ) Ribeirão das Lajes-Rio Santana, and the first domain, at north of this DCZ, is composed of the deformed granitic rocks of the Serra das Araras Batholith (Sad & Barbosa, 1985). The second is mainly constituted by a banded orthogneiss with intercalations of amphibolites injected by pegmatite bodies concordant with the foliation of the country rocks (Figure 1).

The Serra das Araras Batholith has a NE-SW orientation and a steeply dipping (60 to 70°) to NW, limited to the north by the DCZ of Mendes, with vertical dips. These two zones are parallel to the anastomosing DCZ of Além-Paraíba, which is the most important tectonic feature in Rio de Janeiro and is situated to the north of the area. The Litoral Fluminense Domain has a different structural framework from the last domain and is characterized by a more gently foliation affected by axially distinct open folds that affect the Paraíba do Sul Domain.

The South Atlantic Event (Schobbenhaus et al., 1984) affected the studied region in the Early Cretaceous (associated to NE-SW trending tholeiitic dykes swarm); a Hot Spot trail (Sadowski & Dias Neto, 1981) was responsible for the generation of alkaline massifs (associated to ENE-WSW trending alkaline dykes) and since the Paleogene some graben structures were developed, like the Guandu-Sepetiba Sub-Graben (Ferrari, 2001).

Tectonic models proposed for the Cenozoic evolution of the region are not consensual. The regional model proposed for the Continental Rift of Southeastern of the Brazil by Riccomini (1989) considers its genesis as the response to the regional tensional field NNW-SSE since Paleogene, and the deforming tectonic phases of the related basins (Resende and Volta Redonda) involves the reactivation of pre-existing faults, in this order: (1) Left-Lateral in the E-W direction, with NW-SE extension; (2) Right-Lateral, in response to NW-SE compression, of Quaternary age (Upper Pleistocene to Holocene) and, (3) Extension in WNW-ESE, direction in Holocene, followed by E-W compression. Alternatively to this model of Riccomini et al. (1989), Zálan & Oliveira (2005) postulates that the tectonic regime acting since the Cenozoic was extensional, perpendicular (mechanism of pure shear deformation) to a slightly oblique regime, in a gentle sinistral transtension, shaping rhombohedral grabens. Cobbold et al. (2001) postulates the installation, since early Cretaceous, of an oblique rift in SE-Brazil's margin, related to a transtensional stress field (dextral) that may have been reactivated during the Cenozoic. Ferrari (2001), studying the structural evolution of Guanabara Graben, characterized four paleotension fields, with ages from Upper Cretaceous to Holocene, that correspond to four brittle deformation events: Event 1 – Sinistral wrench, from Campanian to lower Eocene, with the Maximum Stress tensor ( $\sigma_1$ ) horizontal, in the NE-SW direction. This stress field would be responsible of the implantation setting of this graben; Event 2 - NW-SE extension, acting during lower Eocene to Oligocene; Event 3 - extension NE-SW/dextral wrench, with the supposed actuation on Pleistocene and, Event 4 - extension E-W, of Holocenic age. The latter author interpreted these data and infers that the Guanabara Graben implantation happened in Paleocene, under a directional stress field, and controlled by an E-W binary. The evolution since Eocene and Oligocene was controlled by a main extension axis in the NW-SE direction. In this way,  $SH_{max}$  and  $SH_{min}$  directions, NE-SW and NW-SE, respectively, were actives between upper Cretaceous and Oligocene, changing positions only in Pleistocene.

All these brittle and ductile deformations were responsible for the generation/reactivation of planar structures/discontinuities, but they have a pattern and are spatially distributed, closed or filled and control the fluvial evolution, geomorphology and influenced, in last instance, landslides occurrence, object of this work. Their understanding is one of the supports to the main hypothesis of this research, *i.e.*, landslides

are more common in moderate to steep hillslopes facing NW when they have approximately the same orientation of the fractures, joints, faults, shear zones and basically, the metamorphic foliation (Figure 2).

### 3. Basics and Methods

Remote sensing data has a significant potential for use in analysis of natural hazards such as landslides. The main source of information for this work was the Digital Elevation Model (DEM) with 90m of horizontal resolution, version 4, obtained in the website of the Consortium for Spatial Information (CGIAR-CSI) and produced with original data from SRTM. Images from Landsat 7 with the sensor ETM+ (Enhanced Thematic Mapper Plus) and from the Advanced Space borne Thermal Emission and Reflection Radiometer (ASTER) were used. Landsat images were available free of charge on the website of National Institute for Space Research - Brazil (INPE). The methods used in this study were performed in the program ENVI™ (Environmental for Visualizing Images) and ESRI-ArcMap™ version 10.1, at the Laboratory of Geological Informatics (LIG-IGc, USP). Geology, hydrology and planialtimetric data were obtained from the databases of the Brazilian Geological Service (CPRM) and of the Brazilian Institute of Geography and Statistics (IBGE) databanks (Silva, 2001).

Heterogeneities of the rocks, in a chemical or mechanical way, have various forms and scales and often controls the mechanisms (causing anisotropy and influencing the disposition of failure) of Mass Movements (MM), especially landslides. Sources of heterogeneity includes: a) micro fabric and mineralogical variations at the material scale; and b) mesostructural features such as relict joints, relict veins, secondary clay seams, relatively less weathered intact rock slabs, irregular zones of contrasting weathering, differentially weathered dykes, core stones, and soil pipes at the field scale. This large variability in type, abundance and scales of heterogeneities, particularly in saprolitic profiles mean that critical features which control stability of slopes may go undetected during investigations (Aydin, 2006).

The properties of discontinuities have great importance in the stability of slopes because they change the shear strength, in a dependence of their position relatively to the direction of maximum stress. Natural discontinuities could be classified in relation to their type: (1) Integral discontinuities – which are discontinuities that have yet to be opened by movement of weathering; they have tensile strength and, hence, a true cohesion. Intact bedding planes, foliation planes, and strongly cemented joints are integral discontinuities. (2) Mechanical discontinuities which have been opened as a response to stress or weathering; they have little or no tensile strength, they generate shear strength and can be divided into (Price, 2009): (i) Bedding, schistosity or foliation planes - these are formed by changes of material or mineral arrangement in the rock; (ii) Joints - which represent strains of tectonic or diagenetic origin and often fall into well-defined sets whose members are oriented essentially parallel to each other; (iii) Fractures – which result from geomorphological features (landslide, creep etc.) and do not necessarily fall into well-defined sets; (iv) Faults and shears – which result from tectonic and geomorphological processes, with shear movement on either side of a shear surface.

Amaral Jr. & Zuquetti (2007) conclude that, inside the considered region, in more than a half of the analyzed occurrences, the material involved in the LSD is a relatively thin mature residual soil (1m thick). The failure of the LSD process begins in a rotational manner, catches the younger residual soil (1m thick) but, when arriving in a saprolite level, it changes the mechanism, acting as a translational slide (shallow planar). Slope deposits are also directly associated with landslides in Rio de Janeiro. On the foothills of the escarpments, as well as in most of the topographic depressions, highly heterogeneous talus deposits can be mobilized. Colluvial deposits observed in other places in SE Brazil, may locally be important in defining critical places, particularly when these deposits are layered (Fernandes et al., 2004).

The role played by geomorphology in LSD processes in southeastern Brazil mainly refers to the steepness parameter, *e.g.*, Cruz (1974), which estimated threshold slope angles of about 22° for the Serra do Mar escarpments. Gentle hillslopes showing low landslide susceptibility were affected by MM, especially debris-flows, during the heavy 1996 rainstorms. This confirms that other topographic parameters must be taken into consideration. Special attention has been given to concave forms (hollows), intensively investigated, including their effects on surface and subsurface hillslopes, hydrology as well as on landsliding (Fernandes et al., 2004).

### 4. Results

Geological discontinuities associated with the Precambrian rocks (deformed in a ductile manner) and structures or the Cenozoic ones (deformed under brittle conditions) and unloading fractures (also

known as sheet joints) play a major role in landsliding within the considered area and have been investigated in the state of Rio de Janeiro (*e.g.*, Barata, 1969; Jones, 1973; Amaral et al., 1992). Frequently, these fractures can be clearly observed within the city of Rio de Janeiro, representing important mechanical and hydrological discontinuities (Fernandes et al., 2004). Granites are capable of storing elastic strains produced inside them during cooling. They are only released when erosion brings the rocks close to the surface, when they are expressed by sheet joints that are closely parallel to pre-existing topography. Further erosion exploits this weakness by a process known as “onion skin” weathering or exfoliation. In its most extreme form, under humid tropical conditions, this results in the formation of immense domes known as ‘inselbergs’ like in the Sugar Loaf, a touristic point in the city.

Amaral Jr. & Zuquetti (2007) estimated for their studied area that 38.57% of the shallow LSD occurs in hillslopes between 20° and 30° and 24.29% from 30° to 40°. We performed our model with the safety value greater than 15°, as suggested by Lee et al. (2004) who consider that, starting with this value, LSD may occur. The latter authors indicate the threshold of the proximity of a lineament for safety from LSD occurrence, and establish the critical value of 50 m. Above this, they consider a very high probability of LSD. It was made a polygon with a less than 50 m distance to the lineaments in the studied region, performing the *Buffer tool* in the ArcMap™. Foliation planes were statistically extracted. For the lithology data was considered the homogeneity of each unit in attitude in the area, performed a transformation from vectors to raster data. The aspect map was obtained from DEM and classified under 9 classes, rasterized using the *3D analyst extension* tool in the ArcMap™, in the function surface analyses/aspect. With all rasterized data prepared (foliation planes and aspect) we utilized the *Raster Calculator* tool in the *Map Algebra* option at the *Spatial Analyst Box*, using the formula:

$$\text{Con} ((\text{“aspect”} = 5) \& (\text{“slope”} = 3), 1)$$

These values in our formula refers to the raster values (“colors”) with the considered zones of intersection of the attributes discussed above, with the same weight. Doing this, the result is a raster map with the regions of interest that we put in a yellow color. Then we performed the intersection between the values with proximities under 50 m (“buffer”) and the lineaments colored in 9 directions groups, all of this over a ASTER false color composite (Figure 3).

An important control on landslide distribution is a conspicuous and strong metamorphic foliation. Thin ribbons of quartz and feldspars mylonites are commonly found in sheared zones. There are pegmatites and quartz veins associated with some metamorphic foliations, creating contrasting zones of strength in materials and permeability. Weathering processes in mica-rich layer promotes the appearance of highly plastic clay.

## 5. Discussion and Conclusions

The area chosen for this study is in the State of Rio de Janeiro, SE-Brazil, famous all over the world for its peculiar natural beauty. However, the area was greatly affected by environmental problems, particularly landslides and flooding, causing many social and economic difficulties. Mapping the high LSD susceptibility areas is nowadays a major commitment of researchers and governmental institutions involved in the field of landslide assessment. We believe that this work is a contribution to this effort by presenting a relatively cheap method of recognition of a few target areas, presenting many natural predisposing factors to these potentially dangerous phenomena at the same time.

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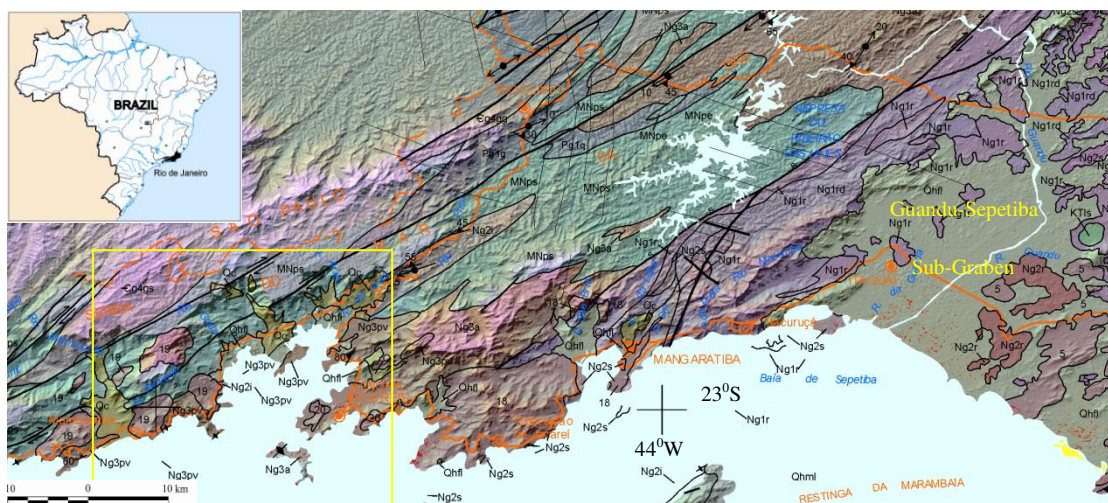


Figure 1. Location and geology of the SE-Rio de Janeiro, and the detailed studied area (yellow rectangle), superposed by a Landsat false color composition. Legend: Unity São Fidélis of Paraíba do Sul Complex– MNps; Rio Negro Complex - (Ng); Serra dos Órgãos Suite - (Ng2s,); Serra das Araras Suite- (Ng3a); Cambrian Granites (εγ5); Cretaceous Alkaline Magmatism (KTλ); Colluvium-Alluvium Deposits (Qh).



Figure 2. Typical shallow landslide in the studied area. Thin soil in steep hill slope facing NW, the same direction of the metamorphic foliation dip. We can also note the banana plantation, very common in the region and factor of slope instability. Location - S22°46' - W43°48', in the Serra das Araras batholith.

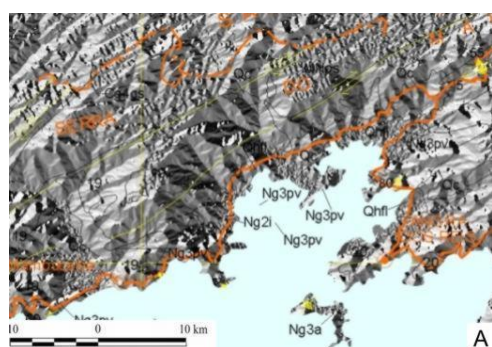
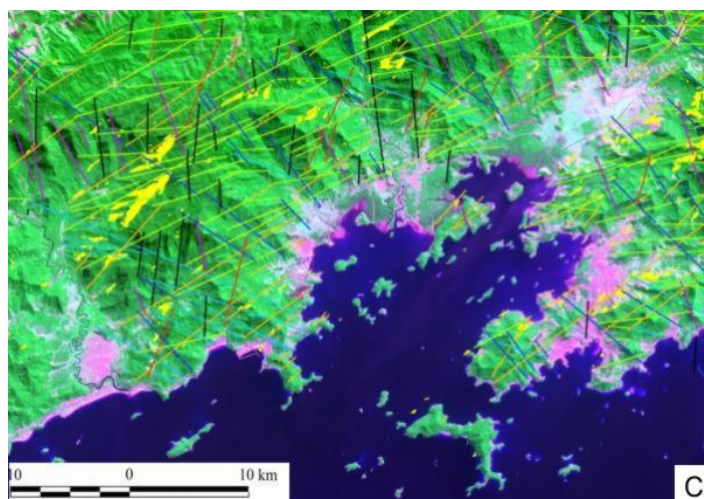
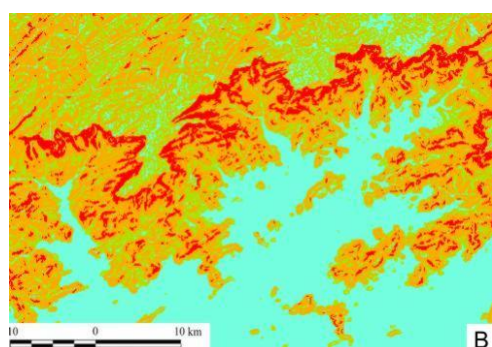


Figure 3. Maps with the resulted operations in the detailed area of Figure 1. A - aspect map of with values (in gray tones) varying from  $0^{\circ}$  to  $360^{\circ}$  where the light gray represents the NW facing slopes and foliation in yellow. B - slope charts with four classes, with light colors  $<5^{\circ}$ ,  $5^{\circ} - 15^{\circ}$ ,  $15^{\circ} - 30^{\circ}$ ,  $>30^{\circ}$ . C - colored lineaments in nine classes, with the buffer distance of 50 m; the yellow areas represent the zones where the foliation attitude and the direction of the dip of hillslopes coincides.



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## ENVIRONMENTAL CONDITIONS ON THE EASTERN PART OF THE CAPARAÓ RANGE NATIONAL PARK AND ITS SURROUNDINGS, ESPÍRITO SANTO STATE, BRAZIL

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**Abstract:** This study is characterized by defining the natural state of water resources facilitating the definition of contaminated sites (naturally) and polluted areas (human influence), establishing the concentration of chemical elements such as Al, Ba, Ca, Cd, Cr, Cu, Co, F, Mg, Mn, Ni, Pb, Ti, Zn, and physicochemical characteristics such as pH, electrical conductivity, turbidity, micro resistivity, dissolved oxygen. Fifty selected points along the Sierra Caparaó were used for this portable multipara meter to realize field evaluation and filtering chemicals, and the results were determined by ICP-OES analysis. The results of the chemical elements measurements were consistent with the limits given in the resolution 357/05 for the classification of special water, but in areas influenced by human activities the physical-chemical parameters do not attend this specification. It is possible to ensure that changes in water quality outside the PARNA Caparaó area have anthropogenic reasons.

**Keywords:** surface water, human activities, element concentrations, conservation unit, Caparaó National Park.

### Introduction

Degradation provoked mainly by the intensive and sometimes abusive use of the natural resources, have increased in sharply in several parts of the world, mainly in the developing countries (Toledo & Nicolella, 2002). The inadequate interventions in the environment have been carting serious problems, mainly for our life quality, as for the environment. Due to the dependence that we have on the natural resources it is necessary to know and to understand all their meanings, since, once modified, removed or destroyed, almost all of the environmental aspects will suffer irreversible changes.

The water comes as the natural resource of great importance for any form of existing life. In this sense, the administration of the water quality (ANA) introduces the federal law no. 9.433 from January 1997 (ANA, 1997), that tends as main goal to guarantee the preservation and availability of the water for its several types of use. This law does not take into account the current situation of the hydric bodies, but the conditions they need to have in agreement with its suitability of bathing.

In agreement with this law and its definitions, three groups to differentiate hydric bodies exist in literature: the fresh water, the salty water and salt brines.

They are classified with respect to its quality and its destination. Waters sources with better qualities do not possess many restrictions in its use, since this doesn't alter their characteristics. Therefore, that is why the determination of the type is necessary and that the physical-chemical-biological characteristics of the hydric resources have to be known.

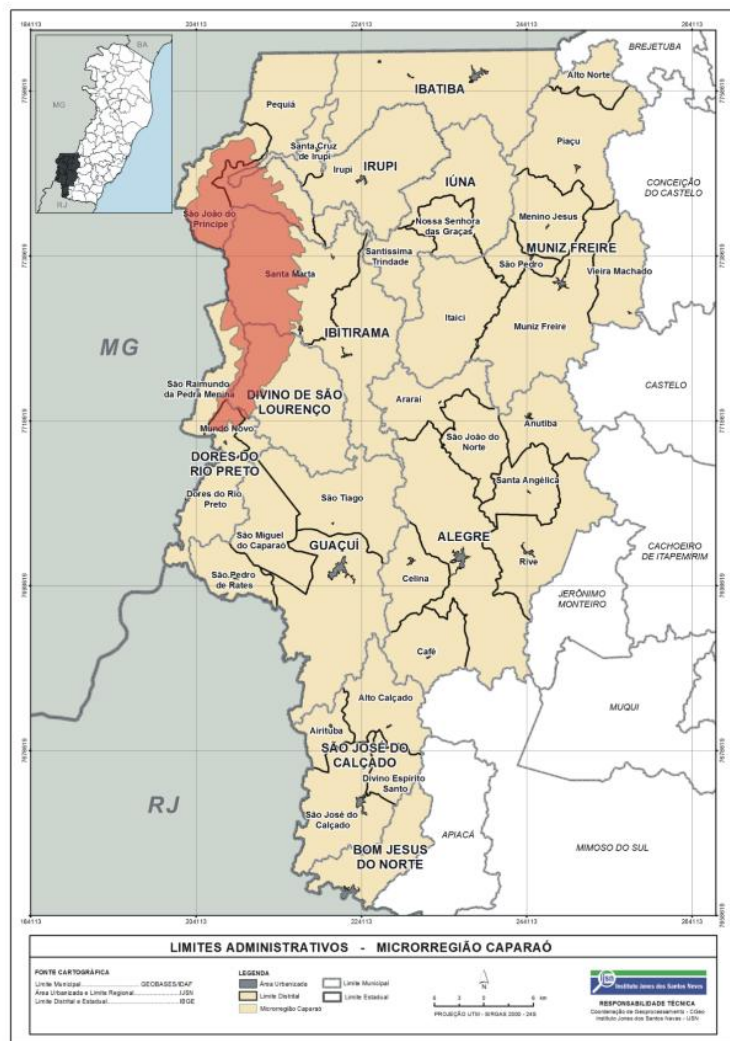
Starting from this, the installation of a chemical (geochemical) background concept is to be done. According to Reimann & Garret (2005) and Reimann et al. (2005) the establishment of the background values of certain elements for an area is crucial, because it allows the separation and specific determination of the geogenic-biogenic contributions to the water quality and separation of natural (water, soils, sediments, plants) and anthropic sources (Fadigas et al., 2006).

In the case of studies in areas, like in the Caparaó region, without direct human impact surrounded by areas with intense human activities, the determination of background values is appropriate to identify possible sources and intensities of human caused pollution s.l.

In cases of found anomalous values the background the contamination caused by human interference can be determined (Rodrigues & Nalini, 2009). The Caparaó range shelters an important National Park, where natural characteristics of the Atlantic Rain Forrest to altitude vegetation are preserved, and exempting of human alteration. This may possible the acquisition of background values may serve as basic parameters for the future evaluations of contamination in this and similar regions.

## Location and characterization of the study area

The Caparaó Range is located at the state boundary between Espírito Santo and Minas Gerais (Figure 1). In this area, the Caparaó National Park installed on May 24, 1961 in agreement with the federal law no. 50.646, area that shelters the Pico da Bandeira, the third highest peak of Brazil. About 80% of the Park surface is directed to the eastern Side, includes seven cities of the Espírito Santo and four of the Minas Gerais State. The limiting coordinates are 20°19' and 20°37' latitude, 41°43' and 41°53' longitude. The surrounding of the Park is formed by the municipal districts of Ibitirama (where it is located the highest point of the Range), Divino de São Lourenço, Dolores do Rio Preto, Irupí and Iúna, Alto Caparaó, Espera Feliz and Alto Jequitibá.



**Figure 1:** Map of the investigated region.

Group and the Paraíba Complex (Horn, 2006). The Neoproterozoic-Cambrian Granitoides are post collisional not deformed (Suites G4 and G5) and occur together with foliated Granitoides belonging to Pre collisional Suites G1 and G3 (Figure 2). The relative proximity of the Mountain Range to the coast evidences great altimetry variation (~3000 to 700m) on a space of only 150 km, (Figure 3; IBDF, 1981).

In agreement with the actual classification (Ab'Saber, 1977), the eastern part of Caparaó Range can be described as a basin, possessing a lot of drainages that dissect the relief in a preferential E-W-direction and on the northern part sometimes with a secondary N-S orientation (IBDF, 1981). This basin contributes to the formation of important rivers of the Southeast of Brazil, especially the Itapemirim, Itapaboana and Doce Rivers (Nunes, 2011).

The interactions of several peculiar factors, like the position belonging to the tropical area, the proximity to the Atlantic Ocean and high topographic variation determine the climatic type of the area. There are two different well defined seasons a rainy one, with frequent high precipitations, and a dry one with sensitive decline of the rainfalls (Horn et al., 2006; Oliveira & Horn, 2007). The localization in the path

The activities at those municipal districts are agriculture and farming as the main economic factor, some digging places and actually grown rural tourism with construction of hotels, lodges and pathways, which changes chemical and physical conditions of soil, water and air.

Geologically, the Caparaó Range is located in the Mantiqueira Province, belonging to the western Border section of the Araçuaí Orogen in the Ribeira Orogenic Belt. It is seen as a very tight, asymmetrical antiform fold structure of kilometric size (Novo et al., 2011). Cunningham et al. (1998) described the Caparaó Range as an zone affected by ductile shear, which exposed this the rocks of this isoclinal west-vergent antiform with north oriented axe.

Cabral (2012) separates three relatively homogeneous lithological units: Basement rocks; Neo Proterozoic Meta-sedimentary Cover; (Noce et al., 2007) and Neo-proterozoic-Cambrian Granitoides (Pedrosa-Soares et al., 2007).

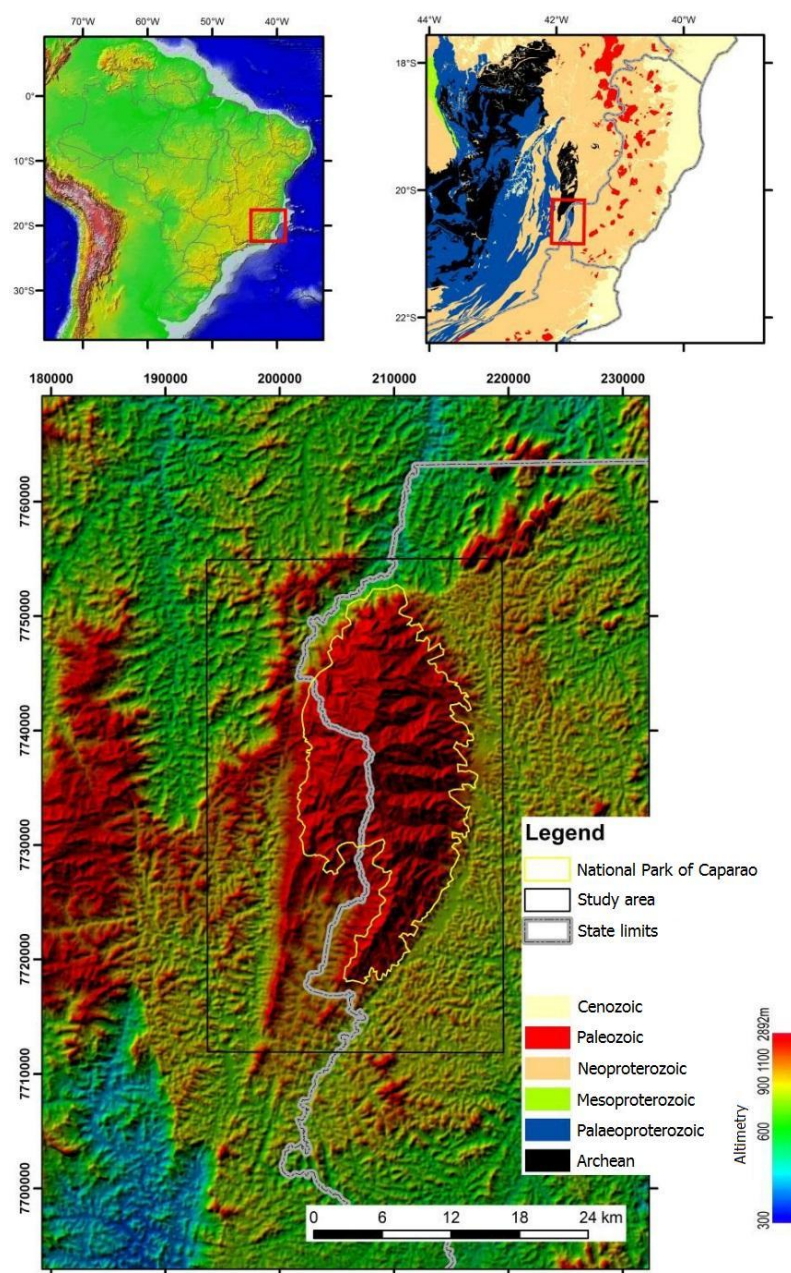
The basement is composing by metamorphosed ortho-gnaisses (Amphibolitic to granulitic Facies).

The meta-sedimentary cover at the South is forming by para-gneisses, similar to those from the Andrelândia

of currents of polar origin is also influenced the situation, which evidence the significant differences between the maximum temperatures registered in the summer and the lowest in the winter. This show the importance of relief variation as an important factor in the annual temperature distribution of the area, determining for winter low to very low temperatures and not permitting very high daily maxims in the summer. For the lowest attitudes the temperature keep around 24°C and decreases to higher ones, getting to be inferior than 0°C at the Instituto Brasileiro de Defesa Florestal (IBDF, 1981) summit.

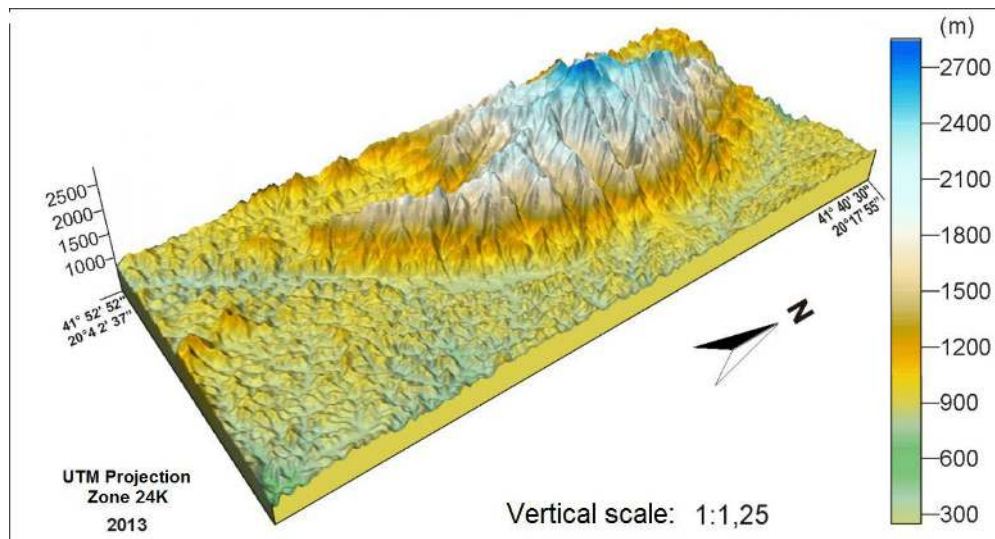
### Objective

The evaluation of the natural state of river water at the Caparaó Range is an objective of this work. Its surroundings, by the determination of the concentrations of selected indicator elements (Al, Ba, Ca, Cd, Cr, Cu, Co, F, Mg, Mn, Ni, Pb, Ti, and Zn), together with the evaluation of physiochemical factors, such as pH, temperature, dissolved oxygen, turbidity, electric conductivity and resistivity. The variation of these parameters along the sampled drainages is correlating with geology, vegetation and climate conditions to obtain background values and indications of intensity and spatial distribution of human contamination.

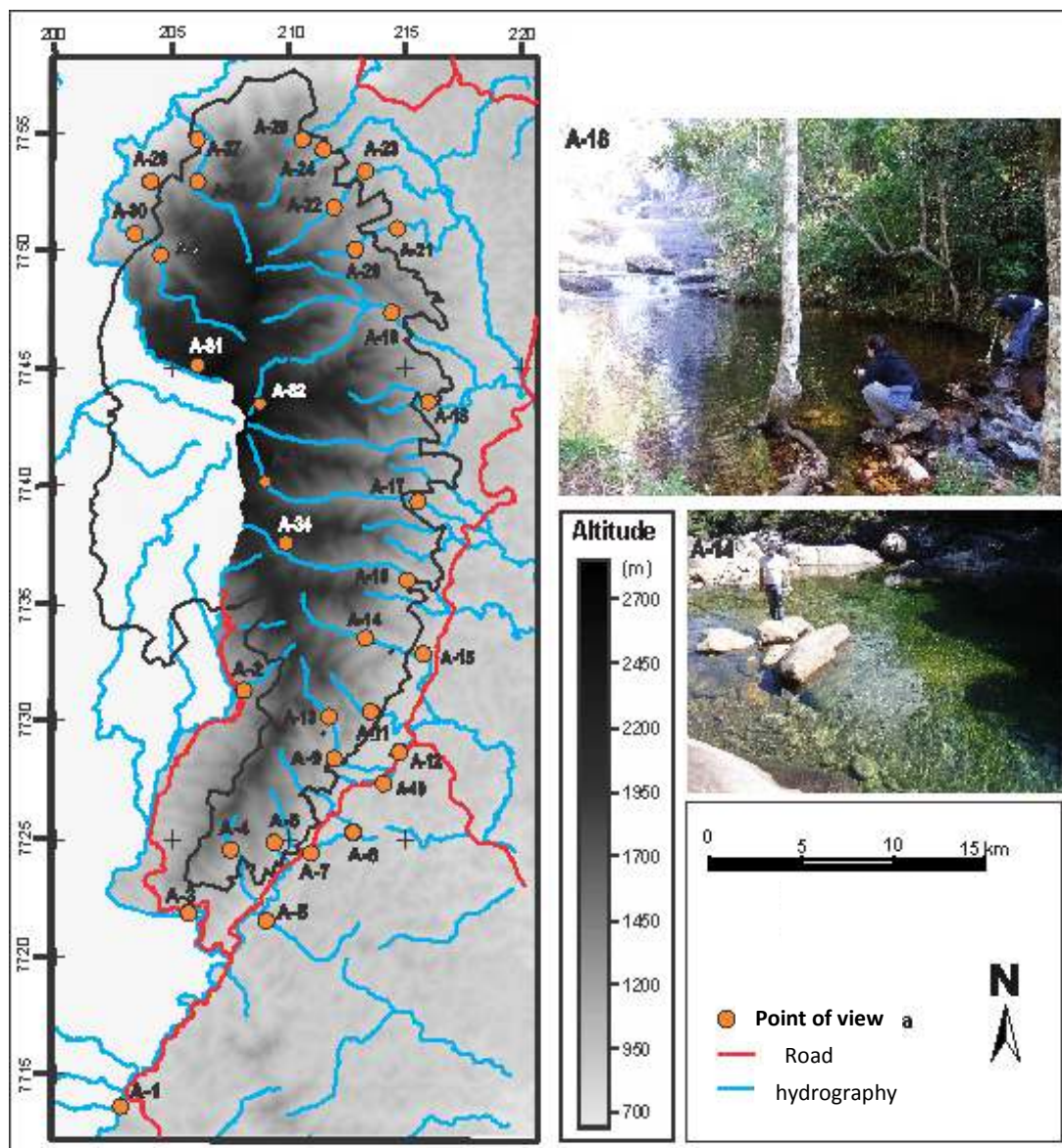


**Figure 2:** Schematic map of the morphologic situation of the Caparaó Range (after Cabral, 2012; modified) , including the Park.





**Figure 3:** Map the geomorphological-geological situation of the Caparaó Range.



**Figure 4:** Digital model image map with the sampling points.

## Methodology

Fifty samples were collected, in the way to cover completely the studied area. Sixteen samples were collected in the drought period (October - 2012), and thirty-four in rainy period (March/May - 2013).

Being declared as a Federal Conservation Unit, it is necessary the request authorization of ICMBio (Institute responsible for Brazilian National Parks), and therefore this research is registered in the National System of Authorization and Information in Biodiversity (SISBIO), under the number 32142-1.

The sampling conditions follows proceedings using bottles of polyethylene of 500ml, previously washed with distilled water and the collected sample stabilized in pH with addition of 5ml of HNO<sub>3</sub>.

The physiochemical parameters (Temperature, Dissolved Oxygen, Turbidity, pH, Electric Conductivity, Resistivity) measured in situ in the field. The collected samples conditioned in thermal boxes, mitigating possible current alterations caused by temperature change.

In the process of sample preparation were used 45µm cellulose nitrate filters using vacuum filtration. For the determinations, it was using a spectrometer of optic emission spectroscopy with docked inductive plasma torch (ICP-OES) the SPECTRO, at the Laboratory of Environmental Geochemistry (NGqA) of the Geological Institute of UFMG.

## Results

The major part of the analyzed samples from the dry period show chemical values and maximum physiochemical data in agreement with the established values in the classification of special water at CONAMA resolution no. 357/2005.

The most samples show also concentration near, or slightly over the detection limit of the used method (ICP-OES) which are in this case Cr: 0.0417 ppm; Cd: 0.0035 ppm; Zn: 0.0044 ppm; Pb: 0.0801 ppm. Only Mg values are higher with maximum obtained about 2.336 ppm and the minimum near 0.571 ppm, for samples collected during the dry period. Some results are showing with the values for point 1 (Figure 4) are 2.335 ppm for Mg, 4.519 ppm for Ca, 2.575 ppm for Fe and 0.2264 ppm for Ni, for sample 6 were found 0.0714 ppm for Cu and 0.0166 ppm for Mn. The sample 3 (figure 4) showed the highest Al value, 0.949 ppm, sample 14 has the highest Co with 0.0442 ppm, 16 for Ba 0.1371 ppm and 8 with 0.0473 ppm for Ti.

With the support of analytical data is possible to identify the degree and type of human interference in this region.

The samples collected during the rainy period have higher turbidity as permitted in law (CONAMA 375/2005) and one point have very low resistivity. All points have chemical values below law limits (CONAMA 375/2005) and sometimes detection limits. The highest values are 0,855 ppm Mg at point 21, 0.25ppm Al, 0.94 ppm Fe and 0.0006 ppm Ba at point 11 and at sampling point 31 0.046 ppm Ti.

It is possible to divide the data in three groups: Environmental pool 1 includes the points with the highest alterations and higher concentration of elements; environmental pool 2 has a wide spectrum of elements, without Ni and the concentration near the natural middle values; and the environmental pool 3 show great a variation on concentration and type of elements.

Some of the determined elements show a peculiar distribution, like Ba with higher concentration in the valleys of Northern-central part with western-eastern orientation and Ni in river parts with higher turbidity.

## Conclusions

The direct area of Caparaó National Park of doesn't show significant indices of contamination and samples collected in the Park were in agree with the Brazilian legislation.

It was able to observe a correlation between physical parameters (pH; turbidity) with rock substrate, soil composition and vegetation. On the eastern side a deposition of air, derived particles can play a role of composition. The water has a slightly acid, reaction, typical for rain forest waters.

In the surrounding of the Park area water is influenced by different human activities and therefore the conductivity, pH, turbidity increases and chemical composition differ.

Element concentration (especially Mg, Al, Ca, Fe) varies considerable between rainy (lower) and dry periods (higher). Trace element concentration show that a monitoring of the areas due to higher human activities like tourism, agriculture, settling and mining are increasing.

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## CHEMISTRY OF MINERALS FROM THE AZEGOUR SKARN DEPOSITS, WESTERN HIGH ATLAS, MOROCCO

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### Abstract:

The Azegour Cu-Mo deposit, located on the north side of the High Atlas, occurs in lower Cambrian volcanic and sedimentary rocks. The mineralization of this deposit is directly associated with skarns, developed on carbonate bars during the intrusion of the calc-alkaline hyperaluminous granite of Azegour. The type of the hydrothermal transformations recorded in the carbonated bars is controlled by the lithological nature of the protolith and is closely confining with the volcanic and volcano clastic levels.

Five paragenetic stages of skarn formation and ore deposition can at least be described: Stage I: clinopyroxene; stage II: wollastonite ± vesuvianite; stage III: garnet; stage IV: quartz ± potassium feldspar ± calcite ± sulphides ± molybdenite ± cassiterite ± scheelite ± fluorite ± accessory minerals (apatite, zircon, titanite) and stage V: amphibole ± calcite ± chlorite ± muscovite ± epidote ± sulphides. Two mineralizations stages are identified. The first stage observed in volcanic and volcano clastic rocks in contact with the dolomitic marble is previous to the metamorphic and structural events and consists essentially of sulphides and sulfo-arsenides (Cu, Pb, Zn, As and Ag). The second stage of mineralization (Mo, W and Sn) is observed in the skarn from marble of granitic metamorphic aureole.

**Keywords:** skarn, mineralization, mMetasomatic, Azegour, High-Atlas, Morocco, Cu, Mo deposit.

## INTRODUCTION

The Azegour Cu-Mo skarns deposit, located about 60 km in the SW of Marrakesh city and about 20 km southwest of the Amizmiz village (Fig. 1), is one of many base and precious metal deposits hosted in the Palaeozoic formations of the north side of the western High Atlas.

It was exploited for the first time in 1921, for copper and thereafter for molybdenum between 1930 and 1946, with an annual average of 200t/j of concentrate with 85% of MoS<sub>2</sub>. The reserves have been estimated at 1.4 to 1.5 Mt ore with 0.2 to 0.7% MoS<sub>2</sub>, 2 Mt of ore with 0.4% WO<sub>3</sub> and 1 Mt of ore with 1.4 to 2.8% Cu. The exploitation works ceased in 1972 but the increase of metal courses in these last years contributed to undertake researches on the site in the perspective of the reopening of the mine in the future.

## 1. GEOLOGICAL SETTING

The regional geology of the Azegour area is marked by a lower Cambrian volcano-sedimentary serie consisting of lava flow and pyroclastites, sandstone-mudstone rocks interlayered with volcanic and pyroclastic rocks, limestone bars and lenses inter-layered with thin pelitic, volcanic and pyroclastic bands or lenses, andesitic flow inter-layered with pelite and volcanic lies (El Khalile et al., 2014). The middle Cambrian is essentially composed of sandstone and pelite (Permingeat, 1957; and Badra et al. 1992). Those Cambrian series are unconformable overlain by the Cretaceous-Tertiary sub-atlasic series. The magmatic activity of Azegour is linked to a volcanic arc context, previously to the Cambrian extension. According to El Khalil et al. (2014) this magmatic activity is a continental intra-plate tholeiite, widely described in the lower Moroccan Cambrian (Badra et al., 1992, Piqué et al., 1995; Ouali et al., 2000). During the magmatism of late hercynian orogeny, small plutons of granite, granodiorite, including the intrusive rocks of Azegour, and other felsic rocks were formed. The Azegour pink granite outcrop is irregular in shape and extends NNW–SSE (Fig. 1), of about 7 km long and 1 km wide, representing a stock that is inclined to the southeast. This Azegour intrusion has a Permian Rb-Sr age ( $271 \pm 3$  Ma) (Mrini et al., 1992). From a chemical point of view, the granite is a K-alkaline hyperaluminous granite of crustal origin (S-type granite) (El Khalile et al., 2014). The calc-alkaline granites of Azegour are associated to molybdenum granites type (El Khalil et al., 2014).



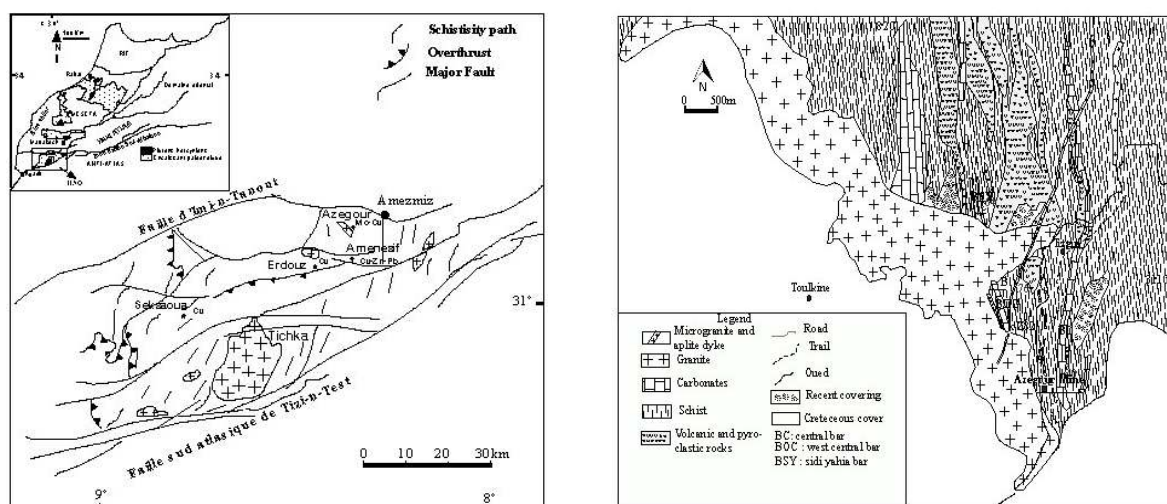


Figure 1: Map of Azegour area; the lower Cambrian volcano-sedimentary series are cut by Permian granites (El Khalile et al., 2014).

Like their counterparts in the Moroccan Palaeozoic massifs, the formations of Azegour have undergone the effect of the major hercynian deformation predating the granite intrusion. Late phases were also described in the area (Ait Ayad et al., 2000).

A thermal metamorphism related to the granite intrusion overlaps the general metamorphism of low grade, which affects the Palaeozoic series of Azegour. It develops a metamorphic aureole of about 1.5 km in the host rocks (Permingeat, 1957). The thermal metamorphism induces recrystallization of carbonate to variant degree (cipolin) with dolomite always as major phase and diopside, humite, green spinel and occasionally scapolite. Other minerals present are quartz, muscovite, also rare ilmenite, and pyrite. Hydrothermal transformations (skarnification) overlap this purely thermal early stage and lead to the formation of pyroxenites, wollastonitites, and garnetite, accompanied with Cu, Zn, Mo and W mineralizations.

## 2. SKARN MINERALOGY

The Cambrian series at Azegour contains four main lens-shaped carbonated bars with variable size, east-west oriented, as follow (El Khalile et al., 2014) : the central bar which has been the object of the old exploitation for copper and molybdenum, the west-central bar, the bar of Sidi Yahia and that of Toulkine situated further to west. The present work carries on the central bar, west-central bar and that of Sidi Yahia which record the maximum of hydrothermal transformations.

In detail, the studied carbonated bars show a heterogeneous composition, varying from pure dolomite, with a few clasts of quartz, to dolomites with pelitic, volcanic and pyroclastic fractions. The type of the hydorthermale transformations recorded in the carbonated bars is controlled by the lithologic nature of the protolith and is closely confined with the volcanic and volcanoclastic levels.

Petrographical and mineralogical textures allow to recognize at least five hydrothermal stages (El Khalile et al., 2014). Early minerals are largely anhydrous, whereas later ones are predominantly hydrous:

Stage I: clinopyroxene

Stage II: wollastonite  $\pm$  vesuvianite

Stage III: garnet

Stage IV: quartz  $\pm$  potassium feldspar  $\pm$  calcite  $\pm$  sulphides  $\pm$  molybdenite  $\pm$  cassiterite  $\pm$  scheelite  $\pm$  fluorine  $\pm$  accessory minerals (apatite, zircon, titanite)

Stage V: amphibole  $\pm$  calcite  $\pm$  chlorite  $\pm$  muscovite  $\pm$  epidote  $\pm$  sulphides.

These transformations draw a well-defined zoning, which repeats at the level of every skarnified bar or carbonated lens. So, from granite (proximal zone) towards the host rock (distal zone), they can be described: Pyroxenites  $\rightarrow$  Wollastonite  $\pm$  vesuvianite  $\rightarrow$  Garnetite  $\rightarrow$  Quartz  $\pm$  potassium feldspar  $\pm$  mineralizations. To these prograde transformations can succeed retrograde transformations inducing the formation of amphibole, epidote and chlorite.

The economic mineralizations of Azegour are represented mainly by local concentration of chalcopyrite and molybdenite associated with scheelite, sphalerite, galena, pyrite, pyrrhotite, and magnetite. Grey copper and silver appear as traces. Some bismuth, uranium and beryllium minerals were also described by Permingeat (1957). The sulphides were oxidized at the surface and subsurface and altered to covellite, malachite, azurite, limonite and hematite. The skarn mineralizations occur as irregularly shaped clusters, pods or thin lenticular bands, following compositional banding. They are most often linked to garnetites.

### 3. MINERAL CHEMISTRY OF THE SILICATE SKARN

In the Azegour deposit, the zonal distribution of the skarn mineral assemblage and mineral composition is very conspicuous. A comprehensive description of the skarn mineral paragenesis is given by El Khalile et al. (2014). Compositional variations of skarn minerals in the different ore-bearing skarn zones are described in the following paragraphs.

#### 3.1 Clinopyroxene

The chemical compositions of the Azegour pyroxenes are summarized in figure 2. Clinopyroxene is essentially a binary diopside–hedenbergite phase with  $X_{Mg}$  ratio ranging from 32.45 to 39.82 in diopside and from 12.02 to 26.07 in hedenbergite; other constituents are Mn, nearly 0.3 wt.% (0.24 to 0.5 wt.%), Al nearly 3 wt.% in diopside and less than 1.59 wt.% in hedenbergite. Clinopyroxene is generally compositionally homogeneous in individual zones.

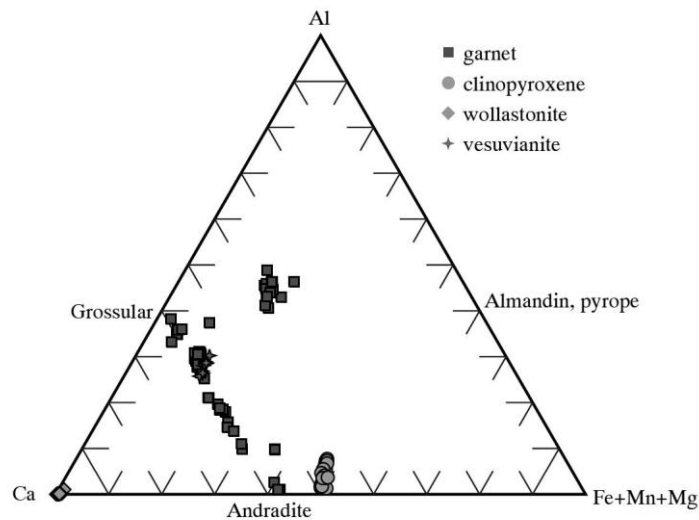


Figure 2: Ca-Al-(Fe+Mn+Mg) diagram showing the chemical composition of minerals from the Azegour skarns.

#### 3.2 Garnet

The compositions of garnet are summarized in figure 3. The proportions of nominal end member molecules were computed after calculating  $Fe^{2+}/Fe^{3+}$  ratio, assuming that  $(Al^{VI} + Ti + Cr + Fe^{3+}) = 2$  per formula unit (p.f.u., 12 oxygen atoms) (Pan and Fleet, 1992).

According to the colour and the chemical composition, four types of garnets can be distinguished:

- 1- Brown to orange grossular type;  $Ca_{2.33-3.1}(Fe^{2+}_{0.037-0.44}Mg_{0.0-0.08}Mn_{0.0-0.08})(Al_{1.37-1.92}Fe^{3+}_{0-0.3})(SiO_4)_3$
- 2- Dark green andradite type;  $Ca_{2.96-3.1}(Fe^{2+}_{0.47-0.51}Mg_{0-0.01}Mn_{0.02-0.03})(Al_{0.05-0.14}Fe^{3+}_{1.58-1.68})(SiO_4)_3$
- 3- Yellowish green to brow-green grandite (garnet of intermediate composition between grossular and andradite);  $Ca_{2.76-3.11}(Fe^{2+}_{0.08-0.57}Mg_{0-0.07}Mn_{0-0.02})(Al_{0.49-1.55}Fe^{3+}_{0.38-1.3})(SiO_4)_3$
- 4- Brown red grossular - almandine garnet  $Ca_{1.59-1.99}(Fe^{2+}_{0.79-1.09}Mg_{0-0.05}Mn_{0-0.02})(Al_{2.032.56}Fe^{3+}_0)(SiO_4)_3$

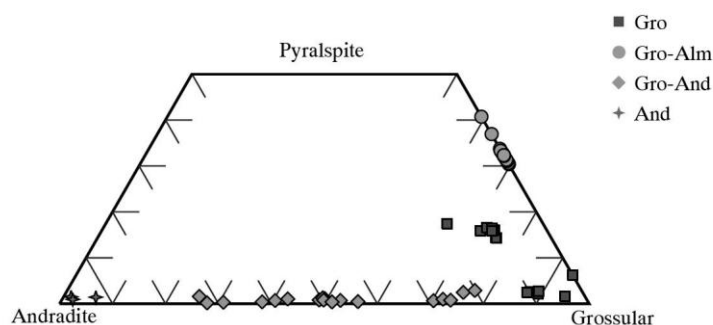


Figure 2: Chemical composition of garnet from the Azgour skarns.

### 3.3 Wollastonite and vesuvianite

The chemical composition of wollastonite is pure ( $\text{Ca}_{5.78-6.02}\text{Si}_{5.96-6.02}\text{O}_{18}$ ) with a low content of Mg, less than 0.2 wt % Fe and Mn less than 0.1 wt%. Two types of vesuvianite were described (El Khalile et al., 2014). The brownish one is formed in prograde stage and is rather rich in Al, Ti and Mg than the late retrograde greenish one, which is rich in Fe.

### ACKNOWLEDGEMENTS

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## THE USE OF DIMENSION STONE CUT RESIDUAL IN AGRICULTURE SOIL CORRECTION. AN EXAMPLE FROM ESPÍRITO SANTO STATE, BRAZIL

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**Abstract** Dimension stone production produce a huge amount of semiliquid waste which contaminates water, air and produce also a visual impact. This fine material has high content of mineral salts and other nutrient. Greenhouse test show that its application increases the nutrients of poor soil and permit to obtain better harvests.

**Key words:** Environmental impact, dimension stone production, lateritic soils, fertilizer, agriculture

### 1. Introduction

From literature is well known the use of industrial waste in different application to reduce environmental impacts. One of these applications is “rochagem” in agriculture (Fontes, 2001). This work shows the applicability of waste material from dimension stone production at Espírito Santo State. Espírito Santo, Minas Gerais and Bahia are the most important producers of Dimension Stones of Brazil. The principal produced materials can be observed from the map of Figure 1. The average annual production of dry residual material by these units is about 165.000 t/y in Espírito Santo State (Brazil ~240.000 t/y; FLUXGEO, verb. com.).



Figure 1. Map of the South-Eastern region of Brazil showing Espírito Santo- and parts of Minas Gerais and Bahia States. The arrow indicates de province capital and center of Dimension Stone Production. The shaded area indicates the principal quarries occurrences.

These materials are principally composed of all type of intrusives (gabbro, granites s. l.), metamorphic rocks like gneisses, migmatites, marbles and quartzites. In Table 1 are shown the compositions of the explored rocks and their average compositions. The waste material represents 20 – 25 Vol% of the whole worked dimension stones and is composed of rock powder, polishing material, quartz sand, limestone, oil and lubrication products, metal powder and parts of the saws and polishing equipment in a semiliquid stage (15-25% water). This water is separated during maturation of the piles and contaminates the environment. Fine powder is liberated after drying and cause air pollution.

Table 1. Average values of elements concentration in the rock powder of the three investigated producers tested for use in agriculture.

	Limagran	Marbrasa	Katugran	
	polishing + cutting	polishing	polishing	cutting
N (%)	-	-	0,02	-
P (%)	0,87	0,38	0,25	0,30
Ca (%)	9,20	1,52	1,27	1,50
Mg (%)	1,30	0,68	3,92	4,56
Zn (mg/kg)	12,70	33,80	6,20	77,80
Pb (mg/kg)	5,50	4,00	2,40	3,90
Cd (mg/kg)	-	-	-	-

## 2. Environmental problems

The waste material is always deposited in the surroundings of the saws and facilities, normally in active river valleys and closed depressions, often without isolation from the groundwater levels. Therefore the environmental problems consist in water contamination and air dust pollution.

## 3. Methods and materials

To be able to use this material for agriculture purposes, a specific grain size is very important (Table 2) because influences the agro-specific chemical parameters, like pH,  $Fe_{tot}$ , nutrient content and percolation velocity in the soil-waste system. The Table 3 shows the nutrient content and chemical parameters of the used soil material.

Table 2. Grain size composition of an average sample of the discarded material from the three industries

Sieves	Limagran	Marbrasa		Katugran
mm	polishing + cutting	polishing	cutting	polishing
1,000	0,00%	0,00%	0,00%	0,00%
0,250	20,12%	6,96%	5,21%	4,51%
0,125	6,48%	2,66%	8,46%	1,95%
0,105	2,65%	1,50%	2,93%	0,50%
0,088	2,06%	1,28%	2,11%	0,31%
0,044	28,92%	18,69%	33,89%	12,83%
Fine	39,77%	68,91%	47,40%	79,90%

Table 3. Chemical and soil parameters of the used soil material.

pH	P	K	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Al <sup>3+</sup>	H+Al	SB	T	t	V	m
	(mg/ dm <sup>3</sup> )		(cmolc/dm <sup>3</sup> )				(cmolc/ dm <sup>3</sup> )		(%)		
Solo	5,40	4,10	110,40	1,10	0,10	0,55	2,60	1,48	4,08	2,18	36,27 32,11

After these preliminary analyses, field experiments were done with three typical Brazilian cultures (beans - *Phaseolus vulgaris* L.; corn - *Zea mays* L.; grass - *Brachiaria decumbens*) with different root depths at the experimental area of UNIVALLE at Governador Valadares.

## 4. Production process

After cutting the rocks in the quarries, the blocks are transported to the stone saws and afterwards to the grinding and polishing tables (Figure 2).

## 5. Results

The results of filtration test are shown in Figure 3, respectively together with the soil-waste properties. All field tests show good results of physical properties for plants grown with the use of the waste material as compared with samples grown without it (Figure 4).



Figure 2. Pictures showing a typical quarry, saw and polishing place. In the places where the waste material is deposited the water content lowers from 80% to 20%. A. Quarry; B. Deposit of blocks; C. Saw; D. Polishing process.

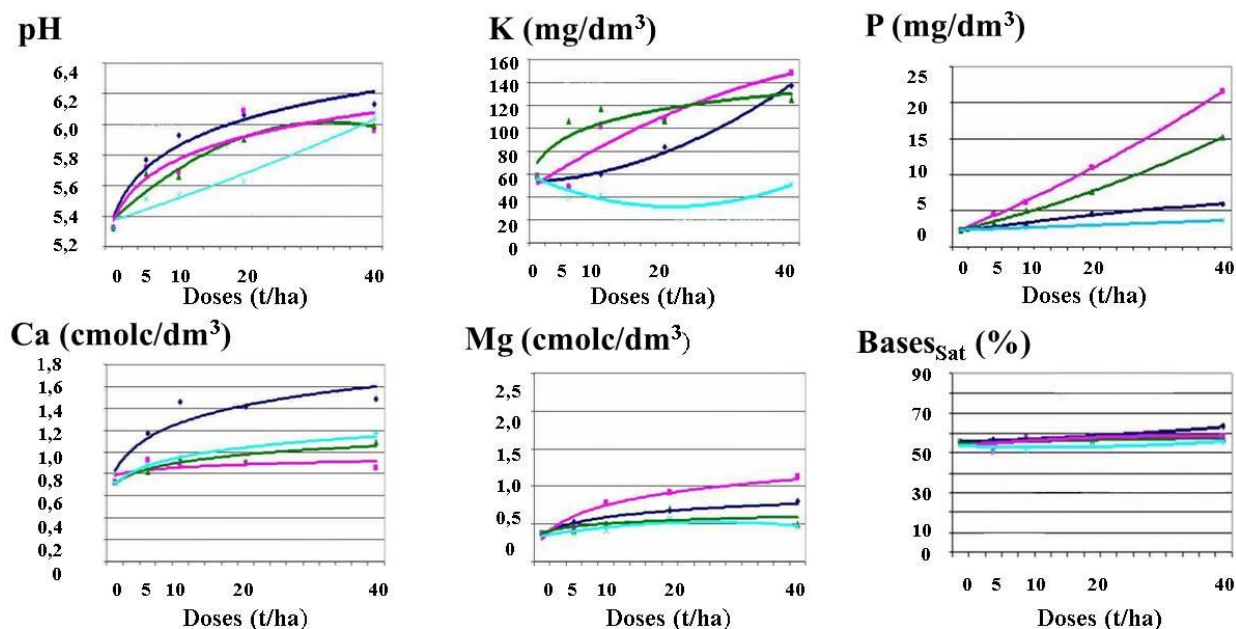
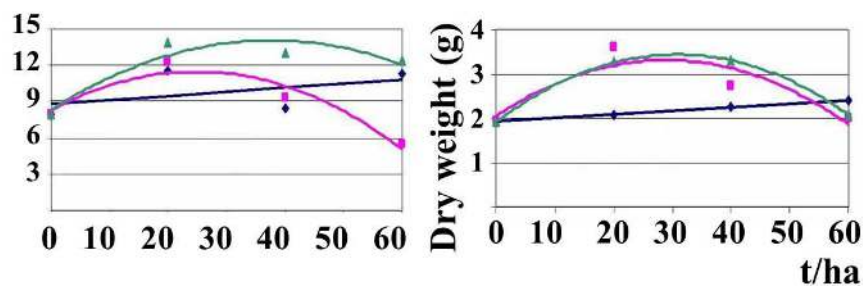


Figure 3. Diagrams representing all chemical parameters for the different soil – waste applications for the investigated four industries for different quantities of waste application.

**Quadrangles:** Katugran; **Triangles:** Marbrasa polishing; **Lozenges:** Limagran cutting+polishing; **x:** Marbrasa cutting;





**Figure 4:** Diagrams of plant evolution with application (dry material).

Left: Whole corn plant (without cobs)

Right: Only grains

**Quadrangles:** Limagran cutting+polishing; **Triangles:** Marbrasa polishing; **Lozenges:** Marbrasa cutting;

## 6. Conclusions and discussions

These results show that the waste material from stone saws and mill can be used due to its composition as correctives and sometimes as fertilizer in agriculture. The example can serve for all countries which have dimension stone production.

## 7. Acknowledgements

The authors thank the UFMG, UNIVALE and FAPEMIG for logistical and financial support. The Association of dimension stone producers supported the fieldwork and gave important informations.

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## CHANGES IN THE P-CONCENTRATION IN BRAZILIAN SOILS AFTER APPLICATION OF WASTE MATERIAL FROM DIMENSION STONE PRODUCTION, BRAZIL

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### Abstract

The use of rock powder from the dimension stone production based on apatite rich igneous rocks is used in this study to enhance the soil quality of poor lateritic soils existent in the Southeastern region of Brazil. The use of this corrective material increases significantly the P-availability in the soil. The material was used in greenhouse- and Freeland tests to increase the grass production and its nutrient quality. In this way the amount of meat and milk products from cattle raising increases and the waste deposits reduces.

**Keywords:** Phosphorous, soil quality, corn production, environmental impacts

### Introduction

According to Acre (2004), solid residue or waste is any substance or discarded material resulting from human or animals activities or sometimes of natural phenomena. It is normally in solid or semi-solid state and includes particulate material.

The solid residues are originated by different human activities, such as metallurgy, chemistry, petro-chemistry, and paper- and food industry among others.

They vary and could be represented by ashes, muds, oils, plastics, you eat, wood, fibers, chemicals, metals, scums, glasses, and more (Naumoff & Peres, 2000), normally deposited in big waste deposits causing longtime environmental problems. The involved costs are very high due to preparation and maintaining of these deposits to prevent soil, water and air contamination.

In the case of dimension stone production, more than 20% sometimes up to 50% of rock mass is transformed in waste paste by cutting and polishing (Moreira et al., 2003), classified like inert residue class III. Therefore this industry creates a great environmental impact which could be reduced by using of this waste in agriculture.

Brazil is passing a crisis due to low international prices of agricultural products, and high national costs caused by expensive fertilizer importation.

Therefore the search for alternatives for fertilization and correcting of the soils of farming, pastures and plantations and to reduce the dependence of these imports is a fundamental piece for the development of agriculture in Brazil by reduction of the production costs.

In the future agricultural activities may have an important participation in the recycling and integration of the industrial materials (s. l.) with introduction in the biological systems, with special view to nutrient rich waste materials (Harter, 1979; King, 1988).

### Methodology

The experiments have been carried out in the greenhouses of the Vale do Rio Doce University at Governor Valadares, MG. For the experiments PVC-tubes of 9.5cm diameter and 35 cm heights have been used. The used soil was collected from textural B-horizon of a red-yellow dystrophic argisil.

Pasty waste from dimension stone production (mainly granites; gabbros and charnockites) from sawmills localized at Cachoeiro de Itapemirim, Espírito Santo State were used.

The material was collected at filtration lakes of the three companies (Katugran, Limagran and Marbrasa), dried in laboratory to values <4% humidity, crushed and sieved for greater particle uniformity. These samples were analyzed and the results are given in Table 1.

The prepared residues were added to the surface of soil filled tubes with different soil-waste relation of 5t/ha, 10t/ha; 20t/ha and 40t/ha, respectively, together with a blind sample (0t/ha) calculated by real tube surface. Then water was added up to 80% of capacity and maintaining for 30 days applications of 20% of capacity.

**Table 1:** Concentrations of mineral nutrients and selected elements in the dimension stone waste.

	<b>Limagran</b>	<b>Marbrasa</b>	<b>Katugran</b>	
	<b>polishing + cutting</b>	<b>polishing</b>	<b>polishing</b>	<b>cutting</b>
<b>N (%)</b>	-	-	<b>0,02</b>	-
<b>P (%)</b>	<b>0,87</b>	<b>0,38</b>	<b>0,25</b>	<b>0,30</b>
<b>Ca (%)</b>	<b>9,20</b>	<b>1,52</b>	<b>1,27</b>	<b>1,50</b>
<b>Mg (%)</b>	<b>1,30</b>	<b>0,68</b>	<b>3,92</b>	<b>4,56</b>
<b>Zn (mg/kg)</b>	<b>12,70</b>	<b>33,80</b>	<b>6,20</b>	<b>77,80</b>
<b>Pb (mg/kg)</b>	<b>5,50</b>	<b>4,00</b>	<b>2,40</b>	<b>3,90</b>
<b>Cd (mg/kg)</b>	-	-	-	-

After this period the soils were sampled in the depths 0-10cm; 10-20cm and 20-30cm to evaluate the percolation capacity of this residue along the profile. The samples were taken three times and analyzed to obtain information about P-distribution and availability. Information was obtained at a matrix of 4x5x3 corresponding to four types of residues, five applied doses and three depths.

### Results and discussion

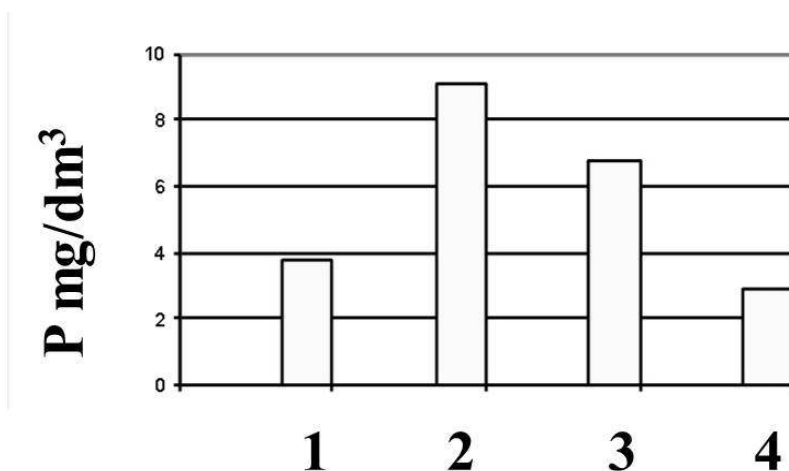
Figure 1 show the medium liberation of P in soil with the application of the residues from cutting and polishing in dimension stone production.

In general, the waste from polishing processes promotes a larger availability of elements in the soil. This is in agreement with the different granulometry of the used materials. The small size material (polishing material) react more easily than the coarser one (saw material).

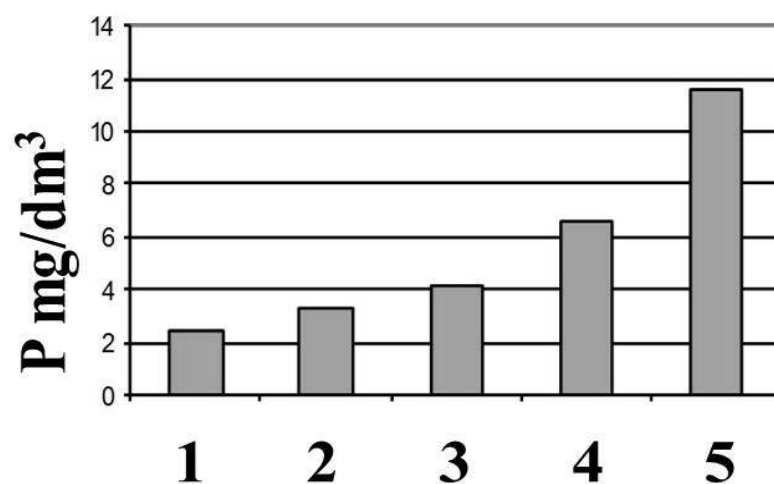
The lowest availability was observed with the residue of Marbrasa sawmill, followed by Limagran residue (a mixture of polishing residue and sawmill), Marbrasa polish waste and Katugran polish waste.

Figure 2 show the relation between P content and waste application quantity.

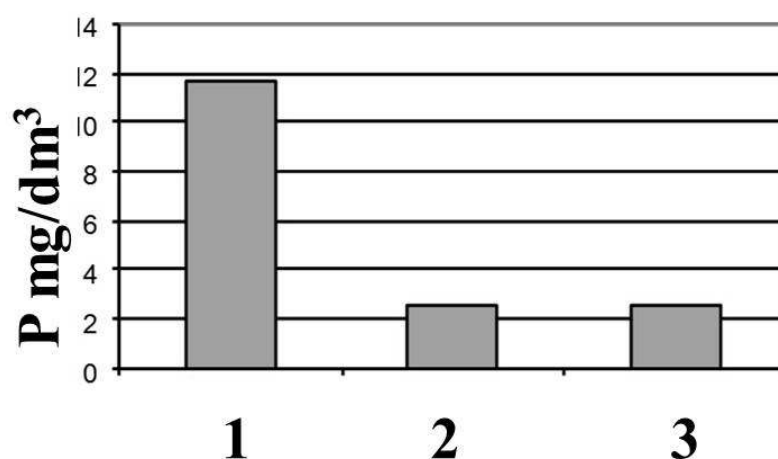
The blind sample has 2,0 mgP/dm<sup>3</sup> and the highest application of 40t/ha increase the concentration up to 12 mgP/dm<sup>3</sup>, values considered high for sandy soils and five times superior in relation to the not treated soil sample. In the soil percolation, independent of the residue type, it was observed that the elements practically were not moved along the profile being characterized by larger amounts in the superior layer of 0-10 centimeters, place where the residue was applied (surface). In the lower layers of soil (10-20cm and 20-30 cm) the P-values of the match levels were similar to the values of the soil testifies. It can be observed also (Figure 3) that the P nearby do not move along the soil profiles and the highest concentration is near the surface. This is very good for grass growing. All samples including the blind one show similar distribution for depths lower than 10cm.

**Figure 1:** Comparison of the P tenor with different waste materials.

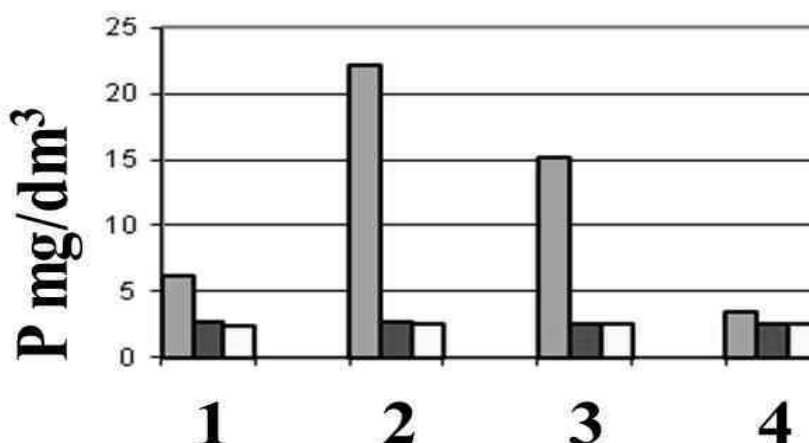
1: Limagran polishing and cutting; 2: Katugran polishing; 3: Marbrasa polishing 4: Marbrasa cutting;



**Figure 2:** Relation between P content in soil and quantity of waste application.  
1: 0t/ha; 2: 5t/ha; 3: 10t/ha 4: 20t/ha 5: 40t/ha;



**Figure 3:** Relation between P-concentration and depths. Middle values for the three industries.  
1: 0-10cm; 2: 10-20cm; 3: 20-30cm;



**Figure 4:** Comparison between P-concentration, soil-depth and industry. The behaviour is near similar. Differences are caused by the different liberation ratio of the saw and polishing material, due to experiment duration time.  
1. Limagran polishing and cutting; 2. Katugran polishing; 3. Marbrasa polishing; 4. Marbrasa cutting;  
Left column: 0-10cm; middle column: 10-20cm; right column: 20-30cm;

## Conclusions

The residues of ornamental rocks production, mainly from granites, charnockites and gabbros, show a high potential to promote the increase of the P-levels of soils, especially near the surface in the upper 10cm.

The finer material (polishing residues) shows a more rapid and complete activity, than the coarser one (sawmill waste). Therefore grinding may be an interest preparation process.

Due to a low mobility the action is very locally, limited to upper parts and annual applications.

## Acknowledgements

The authors thank the UFMG, UNIVALE, CNPq and FAPEMIG for logistical and financial support. The Association of dimension stone producer supported the fieldwork and gave important informations.

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**USO REACTION PRODUCTS OF BATTERY ACID FROM CARS AND CELLULOSE WASTE FROM INDUSTRY AS A NEW FERTILIZER FOR CORN CULTIVATION (*Zea mays* L.) ON POOR SOILS, ON AN EXAMPLE FROM GOVERNADOR VALADARES IN MINAS GERAIS, BRAZIL**

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**Abstract:**

Industry produces a big amount of contaminated sulfuric acid ( $H_2SO_4$ ). After cleaning with micro pore filters the acid is neutralized against  $CaCO_3$  solutions from paper industry producing  $CaSO_4$ . Greenhouse tests show the good performance of this material in agriculture, reducing Al activity, increasing nutrient are more available for the plants. In this way waste deposits are reduced and import costs for fertilizer are reduced as well.

**Keywords:** Industrial waste, sulfuric acid, environmental impacts, fertilizer

**Introduction**

Every country in a globalized world has to struggle against high importation prices of raw materials, world defined alimentation prices, high costs of environmental prevention and mitigation together with the imposition of political-economic facts.

In this sense to create the possibility to lower food costs, enhance the exportation balance and reduce environmental impacts are all very important things.

The possibility to use sulfur acid of batteries and waste from paper mills to produce fertilizer is included in this purposes.

Fertilizers are very important for acid lateritic soils poor in Ca, K, S, P and rich in Fe, Al and Si (Brasilagro, 2011; Collings, 1955).

**Sulfuric Acid**

The sulfuric acid from batteries is a strong acid enriched in heavy metals dangerous for the life. The total production in 2001 was  $165 \times 10^6$ t used in diversificated industry and afterwards liberated to the streams and air.

In fertilizer production (60% of world use) the concentration of  $H_2SO_4$  is about 70% and in batteries ~33,5%.

**Cellulose production**

Cellulose production in Brazil is increasing rapidly (Ribeiro, 2007; Bracelpa, 2010) showing for 2009  $13,5 \times 10^6$ t. Brazil with its extended areas of forests is the fourth world producer of this material. The production of cellulose has as result a big amount of  $Ca(OH)_2$  s.l. which can create a big environmental problem.

**Methodology**

Solid samples were collected from a cellulose and paper industry and the contaminated acid from a recycling industry; both at Governador Valadares, MG. Table 1 shows the composition of these two raw materials.

Table 1. Chemical composition of the substances used in the work.

Sulfuric Acid	Ca-solution
$\text{H}_2\text{SO}_4$ (18%) $\text{Pb}$ , $\text{Pb}^{++}$ , $\text{Cd}^+$ < $\text{Ni}$ , $\text{Zn}$ , $\text{Ag}$	$\text{CaCO}_3$ , $\text{Ca}(\text{OH})^2$ , $\text{Ca}^{++}$ , $\text{Mg}^{++}$ , $\text{S}$

The material was transported to the laboratory of industrial waste research for the purpose of preparing and reaction processing. Figure 1 shows a scheme of the process.

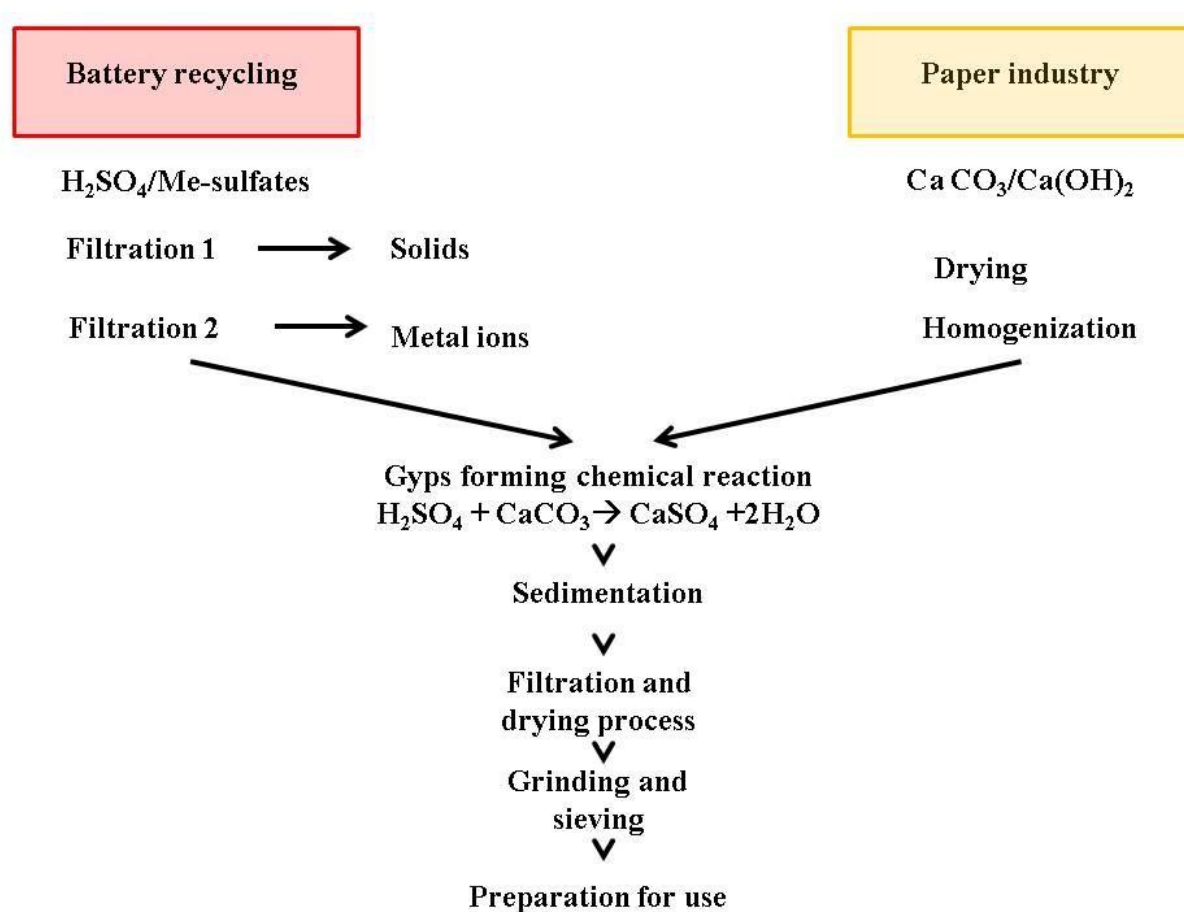


Figure 1. The flow scheme showing the pre-treatment and chemical-physical process for  $\text{CaSO}_4$  production (Piotto, 2003; Almeida et al., 2010)

At the end of the process the material is send to the greenhouse experimental area of UNIVALE agronomic department. There the experiments were realized in pots filled with lateritic soil and different ratios of the  $\text{CaSO}_4$  produced by the process (Figure 1).



**Figure 2.** The different stages of evolution of plants with and without addition of  $\text{CaSO}_4$ .

Samples are taken periodically from the soil and plants to evaluate possible contaminations with heavy elements from the protholiths.

### Results and discussion

- The use of this material allows a better growth of the corn plants (Figure 2).
- The root evolution (rhizome?) is much better and more rapid. The roots reach deeper levels in soil and more contact volume, too, in agreement with Raij (1988) and Sichmann et al. (1982).
- The use in agriculture can nearly absorb the whole acid and residual of cellulose production and reduces in this way water and soil contamination as well as the waste deposits volume on the surface.
- No significant heavy element concentrations were found in eatable parts of the plants.

### Acknowledgement

The authors thank the UFMG, UNIVALE, CNPq and FAPEMIG for logistical and financial support.

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## GEOCHEMISTRY OF SOLID EFFLUENTS AND PHOSPHATE ORE WASHED FROM MÉTLAOUÏ-GAFSA BASIN, TUNISIA

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**Abstract.** The effluent and washed ore show that treatment of ore enrichment is not aggressive. The results are supported by the projection factor, which clearly show the relationships between different elements and mineralogical composition of the effluents and washed ore. The results are a high concentration of 26-35%  $P_2O_5$  (fluorapatite), but it remains carbonates (calcite and dolomite) in low quantity. The apatite show significant REE contents that can be by-product of phosphoric acid. Silicates and carbonates are the major part of effluents. The sulphate and fluoride contents are of the order of 3%, and the  $Na_2O$  content varies between 1 and 1.5%, we observed a good correlation between  $F-P_2O_5-Na_2O-P_2O_5$  and  $P_2O_5-SO_3$ . The levels of Cd, Zn, Cr, V, Ni, Sc, Nb and Cu are from the laundry reject. The maximum values of these elements are in the effluent from the M'DHILLA laundry. The Cd and Zn are found in high concentrations in the solid effluent. The high Cr content is linked with hydro cyclones in chromed steel. The washed phosphate ore was strongly depleted in heavy metals, which were concentrated in the fine fraction released into the hydric network and are thus the main cause of pollution in the region.

**Keywords:** phosphate ores, solid effluents, geochemistry, Tunisia

### 1. INTRODUCTION

MÉTLAOUÏ GAFSA Basin, with areas of exploitation of MÉTLAOUÏ, REDEYEF EDDOUR KEF, MOULARÈS and JELLABIA (Figure 1), is the most important phosphate mining center in Tunisia and is operated by the GAFSA Phosphates Company (CPG). The enrichment of the wet laid phosphate ore and the laundry is done in hydro-cyclones, installed near the production centers. The effluents are present as a fine-grained muds (<70 microns) composed of a small fraction of phosphate, calcite, dolomite, silica, cherts, sulfides and clays. They are discharged into rivers. In this work, we tried to identify these effluents and their degree of nuisance on the environment.

### 2. MATERIALS AND METHODS

Mineralogical proportions of samples of mud were determined by X-ray powder diffraction (XRD with a Pan-Analytical brand X' PERT PRO type) carried out at the Laboratory of the Mineral Resources and Environment of the Faculty of Sciences of Tunis. Argillaceous minerals determination was based on oriented clay slides, using three preparations (untreated, glycolated and heated one hour at 550°C). Mud samples were also analyzed by XRF (X-Ray Fluorescence) for major elements (P, Ca, Si, Al, Fe, Mg, Na, K, and Ti) and ICP-AES (Inductive Coupled Plasma Atomic Emission Spectrometry Activa-Horiba Jobin Yvon Spectrometer) for trace elements (Cd, Zn, Cr, Cu, Ni and Sr) in the Geosciences & Environment Department of Ecole Nationale Supérieure des Mines de Saint Etienne.

### 3. RESULTS

#### 3-1. Mineralogy

Enriched ore from the processing units in Zone L1, Métlaoui 3 and Kef Eddour has a high content of apatite, between 73 and 76% (Table 1). The minerals not eliminated as dolomite, calcite and quartz have low contents and variable with a maximum of 15%. However, the mineralogical composition of effluents includes the same minerals as the products sold (apatite, dolomite, calcite, quartz, opal-CT, gypsum and clinoptilolite). We also noted the presence of sphalerite.

The percentages of each mineral vary depending on the washing units (Table 1). Quartz and feldspar are found in small proportion (8% maximum) as in the ore. The apatite content in washing varies between 19% and 28% depending on the laundry and is very low in sediments of Wadi Thelja River (Table 1).

The solid effluents are composed essentially of smectite and a lesser degree of palygorskite and sepiolite. These non-modified clays, as they shall be reject into rivers. The shape of the X-ray diffraction diagrams (Figure 2) of these effluents is comparable to that of the ore, showing that the plant processes are not aggressive on these minerals.

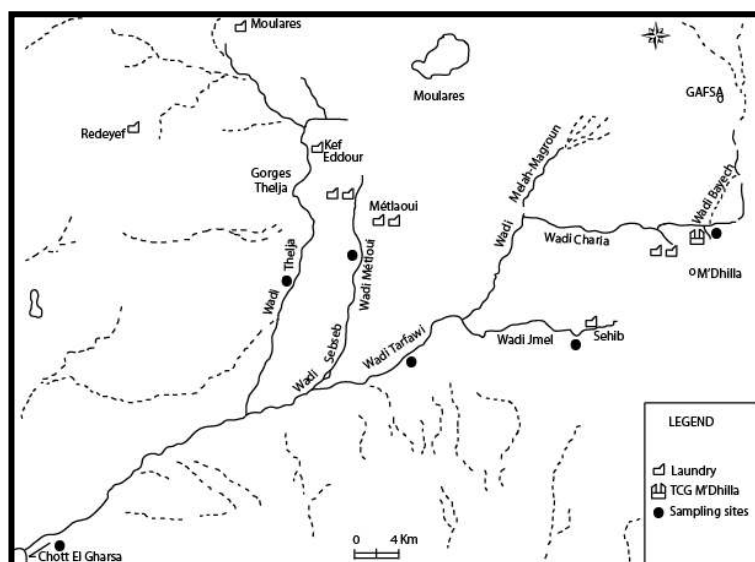


Figure 1: Location of the plant and laundries of GAFSA Phosphates Company (CPG) in the MÉTLAOUI-GAFSA Basin.

Table 1: Semi-quantitative mineralogical composition of washed ore (P) and effluent (R) laundries, expressed in percentage.

	P ZL 1	P MT	P KD	R ZL 1	R MT	R KD	R S <sub>j</sub>
Apatite	73	76	73	19	28	27	14
Dolomite	7	-	14	24	4	3	2
Calcite	15	9	13	20	24	29	53
Feldspars	-	-	-	-	3	5	4
Quartz	-	7	-	6	3	3	8
Opal-CT	-	-	-	13	13	17	12
Gypsum	-	-	-	5	12	3	2
Clinoptilolite	-	-	-	13	13	14	4

Washed phosphate (P) and effluent (R) laundries: Kef Eddour: KD; Métaoui 3: MT; M'Dhilla: MD; Zone L: ZL and sediment (RS) collected from the wadi Thelja River receiving discharges Moulares, Redeyef and Kef Eddour laundries. P: phosphate and R: rejection. (Galfati 2010)

### 3.2. Geochemistry

#### *Washed phosphate ore:*

The enrichment of phosphate in laundries units of Gafsa Basin Métaoui allows to obtain a product rich in apatite with  $P_2O_5$  content ranging from 26% to 31% (Table 2). The CaO values are also high over 45.5%. The ratio  $CaO/P_2O_5$  of the washed ore is similar to that of the phosphorites from Umm El Khecheb with values between 1.59 and 1.73 that essentially allows assigning this element to apatite. The levels of sulfate and fluoride are of the order of 3%, and the sodium content varies between 1 and 1.5%. There is a good correlation between  $F-P_2O_5-Na_2O-P_2O_5$  and  $P_2O_5-SO_3$  (Figure 2).

The maximum  $SiO_2$  content is around 8%, and the silicate fraction is not abundant in the washed ore. The  $Al_2O_3$  contents are low, between 0.4 and 1%; the aluminum is found mainly in the silicates. Iron (0.3 - 0.6%) and magnesium (0.6 - 1.9%) are respectively associated with sulfide and dolomite. The  $TiO_2$  and  $K_2O$  contents are very low. The washed ore is according to the results of XRD, it is mainly composed of carbonate fluorapatite and sodium sulphate.

The Sr (1368 ppm - 2065 ppm) represents the most concentrated element in the washed ore and it replaces Ca in the network of the apatite. Enriched ore is characterized by variable contents of Cd (5 ppm to 27 ppm), however, we observed significant variations in the laundries units between M'Dhilla PMD1 (5 ppm) and PMD2 (27 ppm) compared to the Zone L where the Cd concentrations are very uniform (13 ppm). Zinc shows the same variations (PMD1 189 ppm and PMD2 970 ppm), Cu, Ni (PMD1 12 ppm Cu and 13 ppm Ni), and PMD2 (6 ppm Cu and 5 ppm Ni). However, the levels of Cr and V in the two samples are comparable with those of M'Dhilla but very variable laundry to another (Table 2). Cd and Zn have a similar behavior due to the ease of Cd to enter in the network of sphalerite ( $Zn_{(1-x)}Cd_xS$ ) (Klein &

Hurlbut, 1993; Galfati et al., 2010). In the unwashed ore, the concentrations of heavy metals Cd (13-87 ppm), Zn (58-621 ppm), Cr (119-462 ppm) and Cu (7-35 ppm) are significantly higher (Galfati et al., 2011 a,b). The washed ore is rich in phosphate and strongly impoverished in heavy metals.

The sum of the REE is between 302 ppm and 383 ppm, close to the average ore (147 ppm and 702 ppm). The REE was normalized to upper continental crust (CCS), the normalized REE have values greater than 1 and the ratio  $Dy_N / Sm_N$  varies between 1.37 and 1.62. Distribution curves of REE normalized to the CCS (Fig. 3) show the similarities and the presence of the same negative anomalies of Ce and Sm, and a positive Eu anomaly indicating that REE are associated with apatite and can be by-products of economic interest.

#### Solid Effluents:

The  $P_2O_5$  (5.6% - 11%) and CaO (19.5% - 25%) contents are lower in the washed ore. The ratio CaO/ $P_2O_5$  of the samples varies between 2 and 3.5. This value is much higher than in the washed ore and consistent with the results of X-ray diffraction showing an enrichment of carbonates in the discharge of laundry (Table 1). The  $SiO_2$  (26.36% - 33.5%),  $Al_2O_3$  (5.7% - 8.9%) and  $Fe_2O_3$  contents (2% - 3.2%) are high and correspond to the presence of silicate minerals as quartz, opal-CT, clays and feldspars.

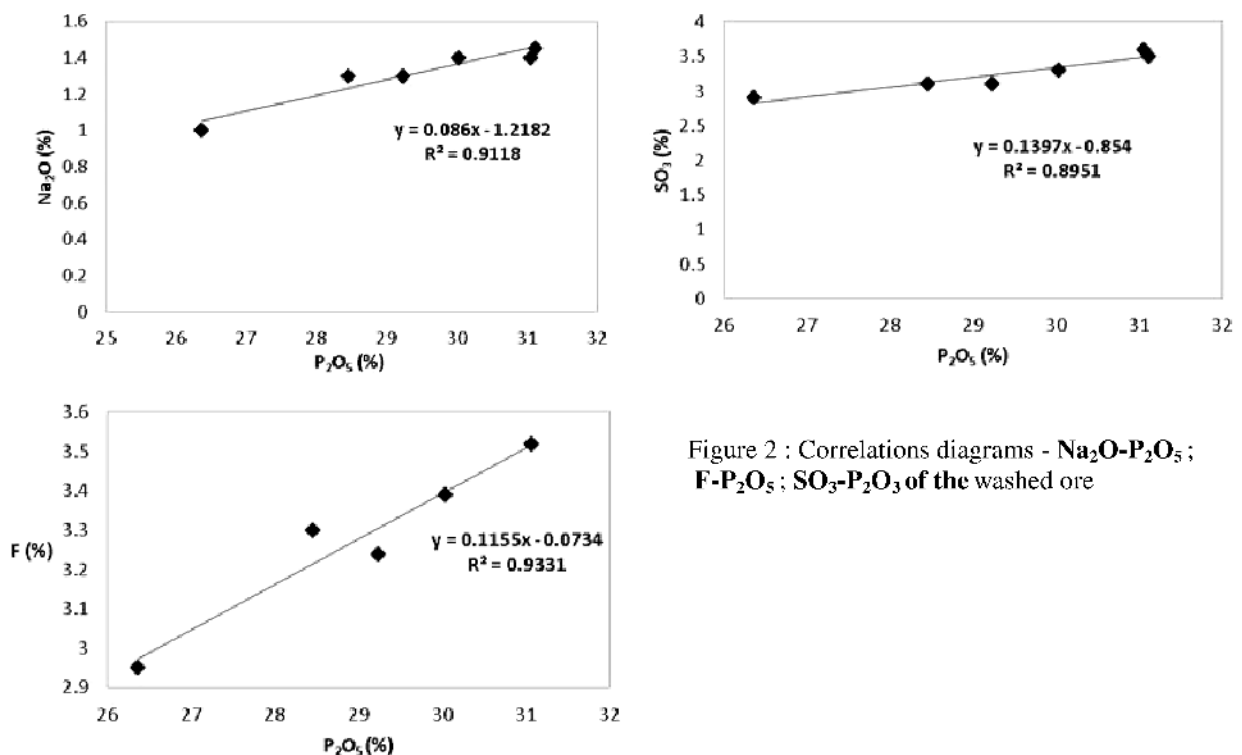


Figure 2 : Correlations diagrams -  $Na_2O-P_2O_5$  ;  $F-P_2O_5$  ;  $SO_3-P_2O_5$  of the washed ore

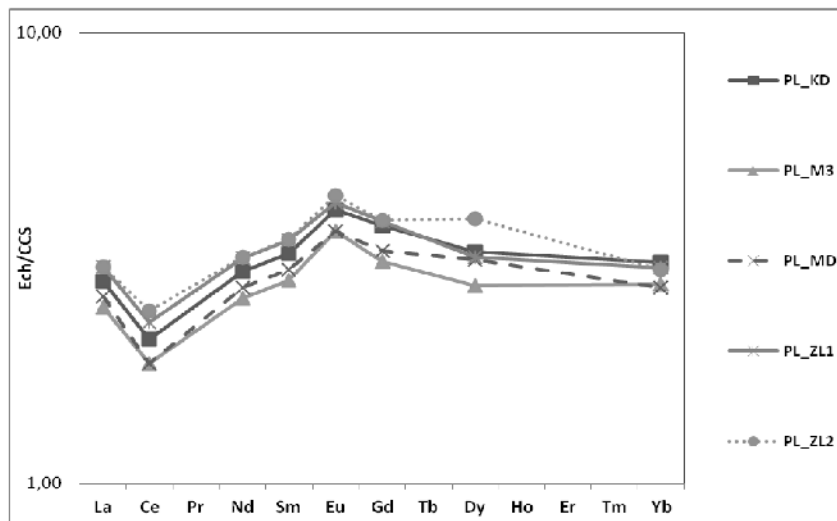


Figure 3: Spectra of REE distribution in washed ore normalized to upper continental crust.

The Cd concentrations are generally higher than in the washed ore, however they are constant in the L laundry zone (13 ppm - 12 ppm against washed ore effluent). Compared to the washed ore the effluents are rich in Zn (200-516 ppm), Cr (209-537 ppm), V (74-210 ppm), Ni (17-34 ppm), Sc (5-6 ppm), Nb (6-7 ppm) and Cu (12-21 ppm). The maximum values of these elements are in the effluent from the M'DHILLA laundry. High levels of Cr may come from the wear of hydro cyclones in chromed steel. The Sr contents in the effluent remained high (594 ppm - 1071 ppm), Sr in being associated mainly with the fine fraction. The REE contents are low between 89 ppm and 182 ppm. The ratio La/Yb is the same order as that of washed ore showing that most of the REE remain in the apatite.

Outside PMD2 and RMD respectively corresponding to the washed ore and laundry effluent M'DHILLA, we have a good correlation between Zn and Cd (0.79). The correlation matrix between major and trace elements of effluents and washed ore shows a weak positive correlation between Cd and Zn with  $r = 0.42$ . The Cd and Zn have a very low negative correlation with  $P_2O_5$  (-0.36 and -0.06 respectively). These negative values indicate that Cd and Zn are not linked to apatite.

The correlation matrix shows a good correlation between Cu, Ni, Sc, Cr and Nb and  $Al_2O_3$ ,  $SiO_2$ ,  $TiO_2$  and  $Fe_2O_3$ . Cu, Ni, Sc, Nb and Cr are associated with clays and sulphide. Sr and Ba show a negative correlation between them; the Ba is associated with silicates, it shows a positive correlation with  $SiO_2$  (0.58 correlation coefficient) and  $Al_2O_3$  (0.56). The Sr, Y, Th and  $P_2O_5$  are perfectly correlated and confirm our observations of their incorporation in the apatite. These results are supported by the projection factor, which clearly show the relationships between different elements and mineralogical composition of the effluents and washed ore.

#### 4. CONCLUSIONS

The effluent and washed ore show that treatment of ore enrichment is not aggressive. The results are a high concentration of 26-35%  $P_2O_5$  (fluorapatite), but it remains carbonates (calcite and dolomite) in low quantity. The apatite show significant REE contents that can be by-product of phosphoric acid. Silicates and carbonates are the major part of effluents. The levels of Cd, Zn, Cr, V, Ni, Sc, Nb and Cu are from the laundry reject. The maximum values of these elements are in the effluent from the M'Dhilla laundry. It may be noted that the Cd and Zn were leached from the ore and is founding in high concentrations in the effluent. High levels of Cr may be from the wear of hydro cyclones in chromed steel. The washed ore was strongly depleted in heavy metals, which are concentrated in the fine fraction released into the hydric network and are thus the main cause of pollution in the region.

#### ACKNOWLEDGEMENTS

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## THE POTENTIAL HAZARD INDUCED BY HEAVY METAL CONTAMINATION RELATED TO TAILINGS PONDS. CASE STUDY: PÎRÂUL CAILOR TAILING POND (SUCEAVA COUNTY, ROMANIA)

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**Abstract:** Tailing ponds are seen today both as polluting factors and mineral resources. Almost all the tailing ponds from Romania have oxidation zones; therefore they have a critical quantity of metals which can pollute the environment in the near future. In the case of Pîrâul Cailor tailing pond (Suceava County, Romania), 49%, 16% and respectively 56% of the Cu, Pb and Zn stock within the oxidation zone is mobile. These percentages represent quantities of 264,489.42 kg Cu, 264,616.26 kg Pb and 899,095.15 kg Zn estimated as being potentially mobile within the tailing pond in a short period of time. This stock is susceptible to be responsible for the short term pollution by migration in the surrounding environment through different fluxes.

**Keywords:** tailing ponds, sequential extraction, heavy metals stock, short term potential hazard

### Introduction

Tailing ponds are seen today both as polluting factors and mineral resources. Investigating their properties, calculating their volumes, evaluating their metal stocks and their acid drainage potential are critical issues both for the industry and the environmental agencies. The tailing pond's internal chemistry and structure depends on the original processed material, the processing methodology and the age of the dumped material. An integrated analysis of geophysical and geological methods can bring fast and efficiently quality information (Iacob et al., 2009).

The goal of this study is to evaluate the hazard potential for heavy metal contamination by integrating geophysical and geochemical methods.

### The hazard of heavy metal contamination

The hazard of heavy metal contamination depends on the stocks of metals, on the fluxes of outgoing elements, and on the retention time of the elements (ratio between stock and sum of fluxes). The hazard is associated with the mobility of metals. Jianu et al. (2012) differentiate between short term and long term hazard. Short term hazard of a contaminated area exists when the stocks of metals are small and the intensity of metal's export is high. Long term hazard depends on the stocks of metals and on the dynamics of internal and external physico-chemical conditions.

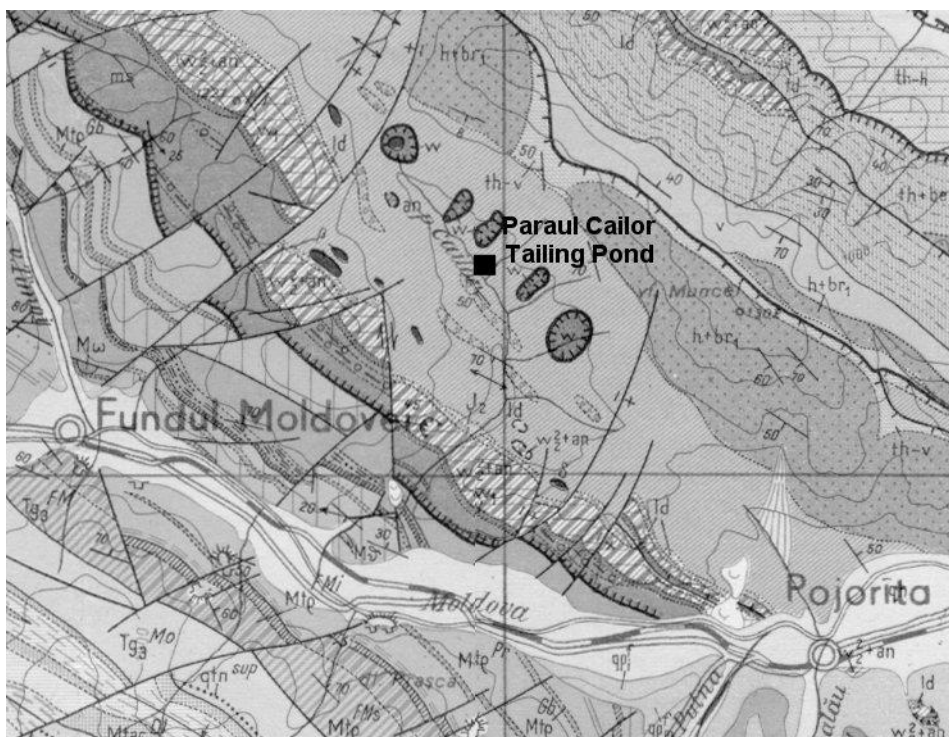
The volumes of the tailing ponds and metal stocks can be calculated by integrating geochemical information from shallow drills and DC resistivity surveys (Radu and Iacob, 2011; Iacob, 2012).

A rapid evaluation of the mobility of metals in contaminated wastes and soils can be done by the so called speciation analysis. Sequential extractions schemes are considered an essential tool in establishing element fractionation in both soils and sediments. Speciation of metals can help in assessing how strongly they are retained in the waste material and how easily they may be released into environment.

### Materials and methods

Pîrâul Cailor tailing pond was chosen as case study for this research. The dump is located in northern part of Romania, close to Pojorâta Town, Suceava County (Fig.1). This is a cross-valley impoundment, and the tailing material resulted after processing the Cu, Pb and Zn deposits from the region. The tailing was built on Pîrâul Cailor River; it has about 400 m in length and 30 m in height.

Through geophysical investigations a volume of 945,343 m<sup>3</sup> has been calculated (Iacob, 2012). The same study identified the separation limit between the oxidation and the reduction zones.



**Fig.1.** Map showing location of the Pirăul Cailor tailing pond (after Krautner et al., 1975).

Metal stock ( $S_M$ ) were calculated according to formula  $S_M = V \times c \times \rho$ , where:  $V$  = volume ( $m^3$ ),  $c$  = content of metals (ppm),  $\rho$  = density ( $g/cm^3$ ). The calculated volume for the oxidation zone was  $519,498 m^3$ , and the one for the reduction zone was  $425,845 m^3$  (Iacob, 2012). A medium content of 414 ppm Cu, 1261 ppm Pb and 1225 ppm Zn was obtained by ICP analysis. Therefore, the total stock determined for a medium density of  $2.5 g/cm^3$  was 978,311.84 kg Cu, 2,980,164.7 kg Pb and respectively 2,896,011 kg Zn.

For the sequential extraction analysis the samples were collected from the oxidation zone. Sequential extraction was performed on samples collected from land surface, 3 m and 5 m depth. All the samples were analyzed by ICP.

Metals adsorbed and/or complexed (i.e. metallic oxides, hydroxides, amorphous aluminium silicates and humic substances) possess reactive surfaces on which heavy metals tend to be selectively adsorbed. To quantify the concentration of heavy metals in this form it is necessary to use an extractant able to form particularly stable bonds with these elements. Salomons (1995) relates metal speciation to potential relative mobility with the following distinction:

Specific phases	Mobility under the normal geochemical conditions
Exchangeable Cations and Carbonates	High mobility
Metals Associated with Hydrous Oxides of Iron and Manganese	Medium mobility
Metals Bound / Fixed Inside Organic Matter	Medium mobility
Metals Bound / Fixed Inside Mineral Particles	Low mobility
Metals Associated with Sulfide Phase	Strongly dependent on environmental conditions
Metals Associated with Silicate Phase	Unlikely to be release

In this study, a four stage extraction method was used to acquire the followings: exchangeable species (stage I), reducible species e.g. bound to Fe/Mn oxyhydroxides (stage II), oxidisable species e.g. bound to organic matter (stage III) and residual e.g. primary sulfides (stage IV) .

## Results and discussion

The sequential extraction analysis revealed the content for each stage for Cu, Pb, Zn and also their weighting in the known geochemical context (Fig.2).



By analyzing the charts from Fig. 2, we can observe that a considerable quantity of Cu can be found in the mobile fraction: 25% as exchangeable cations, 9% as heavy metals associated with iron and manganese oxyhydroxides, 16% metals bound/fixed inside organic substances and 51% as residual fraction.

An important weight of Pb can be found in primary sulfides fraction. The other speciations are present in small quantities: 3% exchangeable cations, 12% metals associated with iron and manganese oxyhydroxides and 1% metals bound/fixed inside organic substances.

In the case of Zn, more than 50% can be found as mobile fraction: 25% as exchangeable cations, 16% as metal associated with iron and manganese oxyhydroxides and 15% as metal bound/fixed inside organic matter.

The obtained percentages from the total content within the oxidation zone was 49% mobile Cu, 16% mobile Pb and 56% mobile Zn (Fig. 3).

Knowing both the mobile element content and the volume of the oxidation zone it was possible to calculate the metal stock within. This stock is susceptible to be responsible for the short term pollution by migration in the surrounding environment through different fluxes: mobilization of metals by atmospheric fluxes or by groundwater fluxes. The mobile element fluxes modeling will be discussed in an upcoming paper.

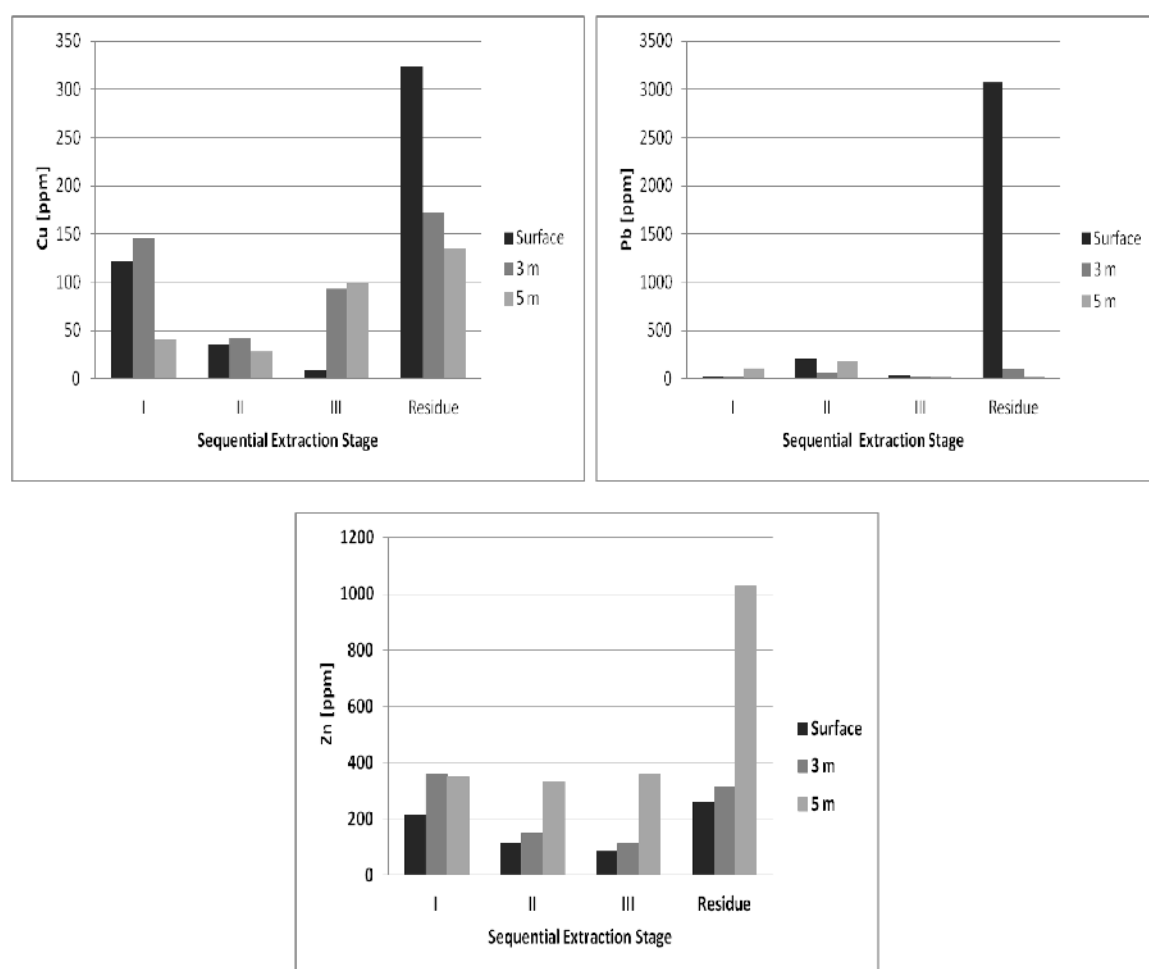
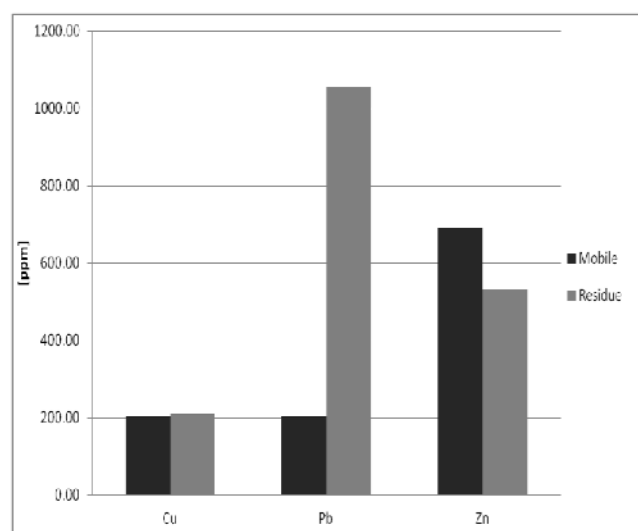


Fig.2. Cu, Pb and Zn content (ppm) for each sequential extraction stage.

Within this study we have estimated the potential hazard to heavy metal pollution on short term. We were able to calculate the mobilization of a quantity of 264,489.42 kg Cu, 264,616.26 kg Pb and 899,095.15 kg Zn in a short period of time. These values represent percentages of 49% Cu, 16% Pb and 56% Zn from the total stocks for each element. This means that the tailing pond has pollution potential in the future almost the same in the case of Cu and Zn and four times more in the case of Pb.



**Fig. 3.** Mobile and residual concentrations (ppm) for Cu, Pb and Zn within the oxidation zone.

### Conclusions

The short term heavy metal pollution does not depend directly on the waste material volume or on the total metal stock, but on the mobile metal stock.

The total metal stock is very important for the long term previsions, namely the long term hazard calculation.

Almost all the tailing ponds from Romania have oxidation zones; therefore they have a critical quantity of metals which can pollute the environment in the near future. In the case of Pîrâul Cailor tailing pond which has been chosen for this study, 49%, 16% and 56% of the Cu, Pb and Zn stock within the oxidation zone is mobile. These percentages represent quantities of 264,489.42 kg Cu, 264,616.26 kg Pb and 899,095.15 kg Zn estimated as being potentially mobile within the tailing pond in a short period of time.

In the future the pollution potential of the tailing pond is higher than the present one. This means that a strategy for both the diminution of the present pollution and of the future risk factors is absolutely necessary.

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## PRELIMINARY DATA REGARDING SANDS HEAVY MINERALS FROM THE LEVEE LETEA (DANUBE DELTA)

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**Abstract:** Levee Letea sands occupy a notable territory in the north-east of Danube Delta. Grain size that prevails is medium sand. The source area of the material (in accordance with the grain size parameter Skewness) is mixed (fluvial and sea). The sands contain a relatively high variety of minerals: silica is prevailing (quartz, calcadony, opal) and is succeeded by feldspars, carbonates, muscovite and heavy minerals (garnet, zircon, titanium oxide (rutile and anatase), ilmenite, magnetite, goethite, staurolite and apatite)). XRF investigations record the prevailing of the major elements (Si, Ca, and Fe), succeeded by minor elements (K, Ti, V, Mn, Cr, Zr, Ni, Zr, Sr).

**Key words:** Danube Delta, levee Letea, heavy minerals, sands, titanium oxide, garnet.

### 1. Introduction- History of the formation of Danube Delta

Danube Delta was formed on a gulf of the Black Sea after an evolution that followed several steps, in time of the vertical sea level changes, by flooding the land through marine transgression or by regression. Deltaic deposits were formed in both cases by marine transgression and regression.

Owing to this fact, the deltaic territory is situated on the crustal fault Galați - Sf. Gheorghe, an area with a high mobility, which had and has as a consequence, internal processes of subsidence and accumulation of deposits, respectively.

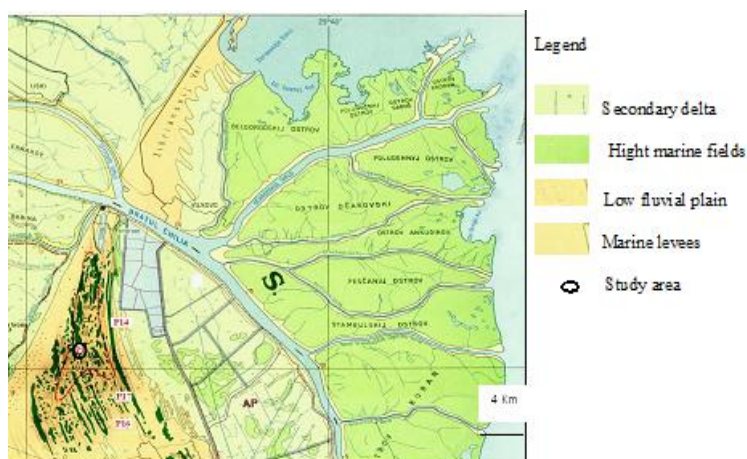


Fig. 1. Letea levee in Danube Delta and Chiliei Delta (Ukraine)

Deltaic deposits, as cover formation, have thickness between 30 m and over 100m (30 m upstream of Isaccea, 40 m at the entrance of the delta, over 60 m at Sulina and over 100 m to Sf. Gheorghe). These deposits are constituted of a succession of lithological complexes having at the base dominantly psedific deposits, which gradually pass to fine material, from coarse sand to sandy silt. To the upper part, there is a lamination with sandy silt that can become plastic clay.

The biggest maritime levees are those which form the “initial belt” (Letea, Caraorman and Crasnicol),

which were formed almost 10.000-11.000 years ago, blocking the deltaic creek and developed the actual fluvial delta. The Letea and Caraorman levees are made up largely of sandy deposits and the most considerable height are in Letea (12.4 m) and Caraorman (7 m) and represent aeolian deposits resulting from the unconsolidated sand deposition.

The study of the heavy minerals from the Danube Delta was undertaken by: Panin and Panin (1969, in Panin, 1989), Coteș (1969, in Gâștescu and Știucă, 2008), Panin (1989) and Panin et al. (1983, in Panin, 1989).

### 2. Materials and methods

We have analysed 50 samples from Letea levee. We have also analysed the grain size, (laser grain size), mineralogy (optic microscope observation and X-ray diffraction) and geochemistry (x-ray fluorescence).

We used 5g from each sample for grain size analysis. The samples were treated with sodium polyphosphate to disperse the particles and then measure using a Horiba LA-950 X-ray grain size particles (Sedimentology laboratory, Bucharest University). X-ray diffraction was done on 1g samples. The samples were made of a fine powder and then analysed using a Panalitical X Pert diffractometer. We identified the minerals from each sample. 1g from each sample was analysed using x-ray fluorescence Horiba XGT-7000 for the determination of elements concentration in the samples. We analyzed on XRF and on polished section.

For the microscopic observation the samples were embedded in epoxy resin and then polished.

### 3. Results

#### 3.1 Grain size

Grain size analysis shows the similarity between the samples. The samples are fine-grained sand and medium-grained sand (Fig. 2).

The mean values are between 1.5 and 2.5  $\phi$  (phi). The distribution is unimodal. The Skewness distribution oscillates around 0 value (-0.3 – +0.3  $\phi$ ) (Fig. 3). Positive skewness (0 – +3  $\phi$ ) and a relatively good sorting are the characteristics of the fluvial sand. Negative skewness (-3 – 0  $\phi$ ) and a good sorting characterize the beach sand. Kurtosis has a platycurtic and mesocurtic characteristic. The dominant kurtosis characteristic is platycurtic. Sorting is good and relatively good (0.35 – 0.7  $\phi$ ), which means a transport over a long distance. Sorting is good at the medium sand and relatively good on the fine sand that was transported in suspension on a short distance. The particles were transported in saltation (fine sand) and traction.

#### 3.2 X-ray diffraction

The samples were separated on grain size fraction. We analyzed every grain size fraction from each samples for the identification of the abundance of the heavy minerals in one of the fraction. Heavy minerals were found in all the grain size fractions analyzed (very fine sand, fine sand and medium sand) (Table 1).

A high quantity of heavy minerals was found in the very fine sand fraction, where we could identify a high variability of heavy minerals. Using X-ray diffraction on the fine fraction (63-125 microns) we identified a part of the heavy minerals (rutile, spinel, zircon, almandine, and andradite).



Fig. 2 Sand- Silt- Clay Diagram

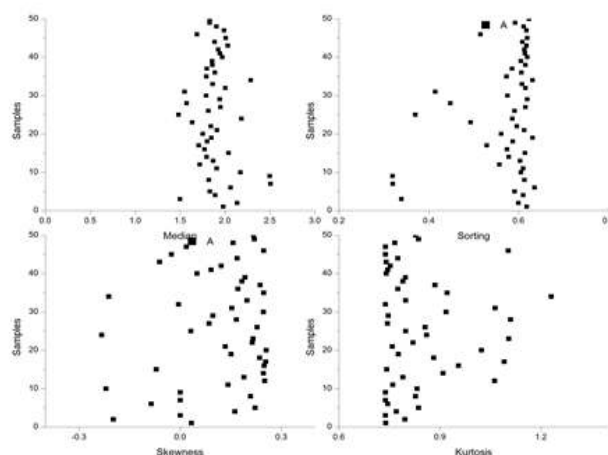


Fig. 3 Grain size parametres

Tabel 1. Heavy minerals from the samples analyzed (on grain size fractions)

G rain size	Quartz	Rutile	Calcite	Spinel	Zircon	Almandine	Andradite	Microcline	Nepheline	Titanite	Ilmenite	Apatite	Garnet	Kyanite	Actinolite	Hematite	Muscovite
Sample 49																	
63-125 $\mu$ m	+	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	+
125-250 $\mu$ m	+	+	+	-	+	-	-	+	-	-	+	+	+	-	+	-	-
250-500 $\mu$ m	+	-	-	-	+	-	-	-	-	+	+	-	+	-	-	+	-

#### 3.3 Microscopy

Microscopic observation consisted of three types of investigation: binocular magnifier, transmitted light and reflected light.

The binocular microscope has been used to determine: roundness (rounded and subrounded) and the variation of the mineralogical composition which consists of quartz, feldspar, carbonates and heavy minerals: garnet, amphibole, zircon, kyanite, staurolite and Fe, Ti oxide (Plate I).

In the transmitted light, the microscopic observation (Plate II) allows the identification of the quartz grainclast, which in most of the cases has wavy extinction, and the presence of the microcline and albite. From the heavy minerals was noticed the presence of garnet and zircon in aggregates or included in quartz joined with rutile. Anthophyllite, sometimes with twinning, also apatite have been identified.

In reflected light we identified two TiO<sub>2</sub> polymorphic minerals (rutile and anatase) (Plate III), as well as ilmenite, sometimes transformed in rutile, magnetite and goethite.

Note that the anatase was often recognized at the microscope thank to its whitish reflexes. Still in the reflected light we observed rarely chromite.

### 3.4. X-ray fluorescence

X-ray fluorescence was performed on the powder of each grain size fraction. On every fraction we measured 3 points. The results indicated the abundance of Si (from silicates and quartz), Fe (from oxidized) and Ca (from carbonates and silicates) (Table 2). The proportions of elements are varying with the spot position on different minerals.

**Tabel 2.** Chemical elements found in the sand grain size fraction.

Sample	Measured points	Si	K	Ca	Fe	Cl	Mg	Ti
63-125 microns	1	57.13			17.39			25.47
	3	86.46			13.54			
125-250 microns	1	58.34	29.29	6.13	2.16	1.07	2.91	
	2	82.53	5.55	6.08	1.80	4.03		
	3	91.05		5.95	0.45	2.33		
250-500 microns	1	65.08		32.43	2.49			
	2	84.14	2.28	11.05	2.53			
	3	89.15	2.65	6.26	1.56			0.37

On the polished sections, we measured 5-8 points on every section, for more reliable results.

In Table 3, can be seen the geochemical similarities between samples. The elements with high concentrations are Si, Fe, Ca and K. The small difference between the concentrations is caused by the mineral analyzed. Remarkable is the presence of Cr, Ti, Mn and Zr.

**Tabel 3.** Geochemistry of the polished sections

Sample	Measured points	Al	Si	Cl	K	Ca	Ti	V	Mn	Cr	Fe	Zr	Ni	Zn	Sr
P8	1		0.92	1.74		96.07				0.64	0.62				
	2		3.4	3.26	0.31	0.41	46.31	2.24	1.89		26.8	15.38			
	3		46.19	1.29	45.5	4.74	0.89			0.35	0.61		0.43		
	4	28.9	28.05	2.88		12.5	0.48		1.59	0.72	23.81			1.07	
	5		97.2	1.29					0.87		0.27		0.37		
	6		50.66			1.84	3.29	0.35		0.77	40.92	1.43			0.74
	7		93.92	3.51							2.56				
	8		88.53	8.38				1.66			1.43				

### 4. Conclusions

Samples from Letea levee are similar from the standpoint of grain size and geochemistry. From the grain size standpoint, the samples are sand (fine and medium) and the sorting is good. More heavy minerals were found in the fine fraction (63-125 microns). Skewness and sorting give us information about the type of the sand (fluvial and marine) and the transport (long distance) of the Letea levee sand. We observed the mixed character of the source, with the domination of the fluvial sand.

From the mineralogical standpoint, it was observed a notable variation of the heavy minerals, dominated by the presence of the iron and titanium oxides. Notable is also the variety of garnet: with chromium (uvarovite), iron (almandite) and probably pyrope. A particularity of these sands is the presence of chromium minerals (chromite and uvarovite).

Regarding the source area, we have underlined the hypothesis of two areas: Carpathian-Dobrogean and Ukrainian cratonic (see the presence of the uvarovite and pyrope).

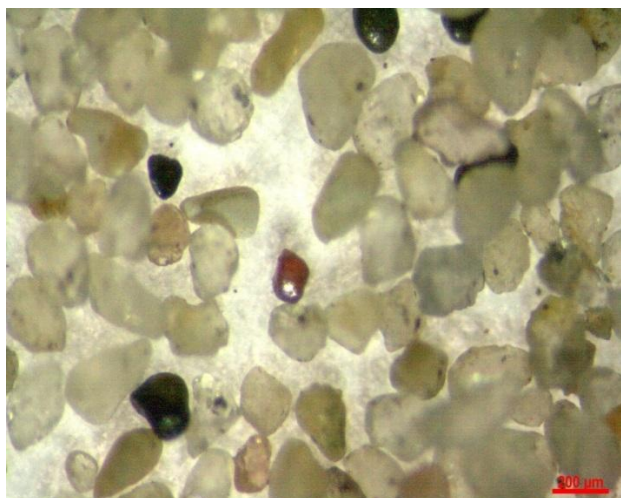
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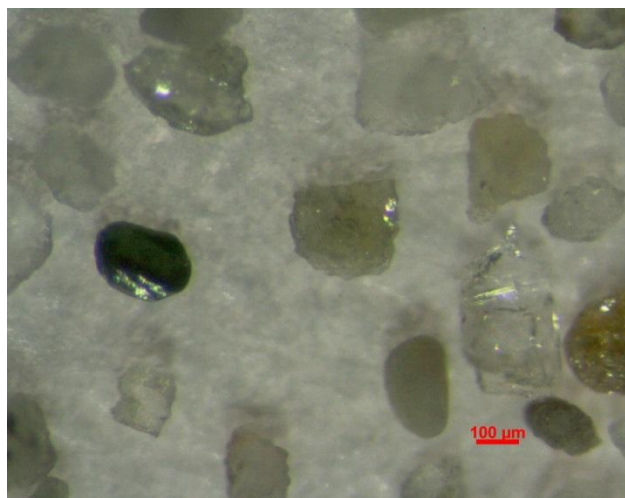


## PLATE I

Binocular microscope images of the heavy minerals from the Letea levee sand. It can be observed the three type of garnet: almandine (red), uvarovite (green) and pyrope (red). Also we found an iron and titanium oxide with metallic luster. The mineral fund is constituted of quartz, feldspar and garnet.



Garnet (almandine) associated with quartz, feldspars and titanium oxide



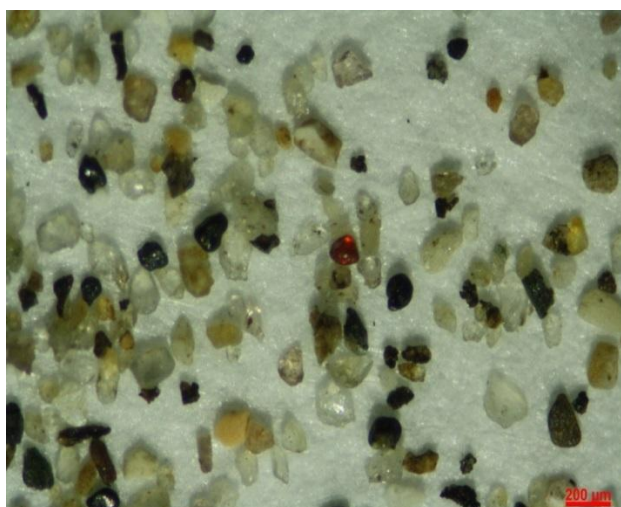
Green garnet (uvarovite) associated with quartz and carbonates



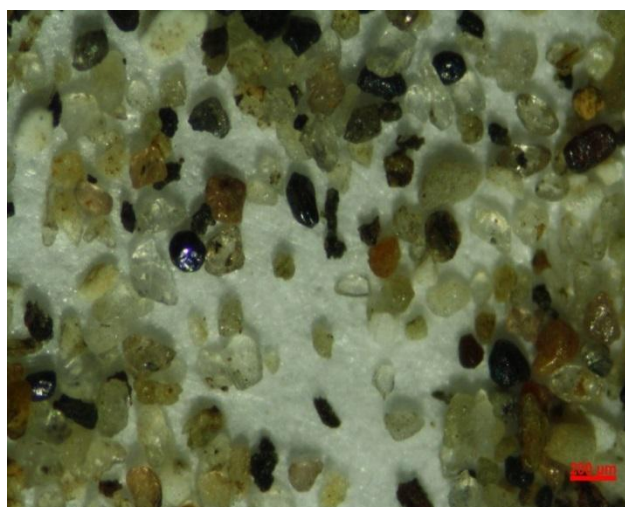
Quartz (amethyst), clast of quartz and bioclast



Idiomorphic apatite, titanium oxide, garnet and quartz



Garnet (pyrope?, center) associated with iron and titanium oxides, quartz, zircon and staurolite

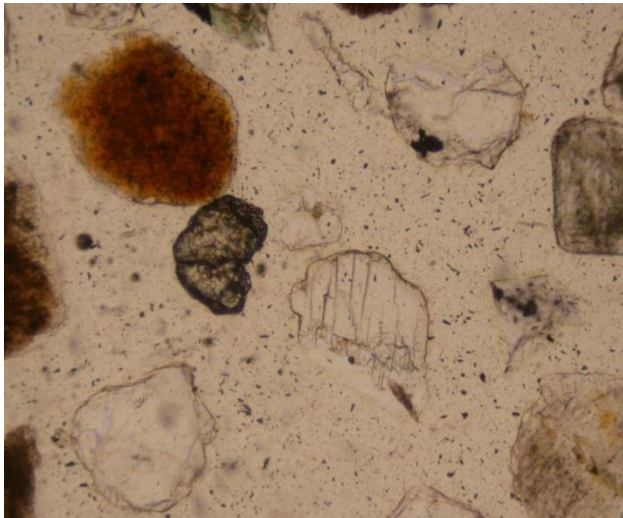


Garnet, iron and titanium oxides, quartz, feldspar and carbonates

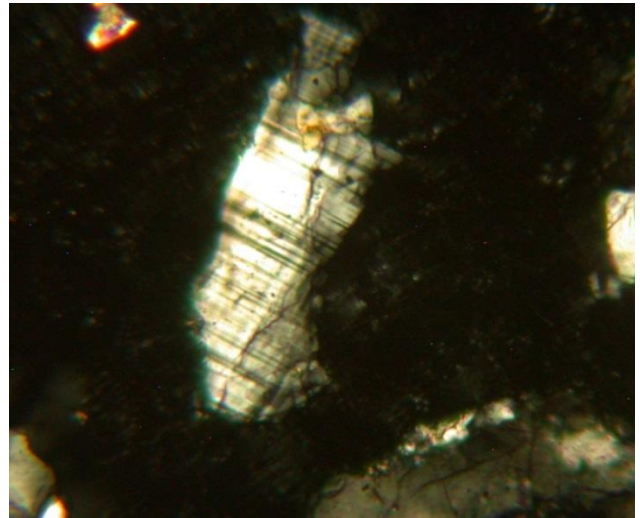


## PLATE II

Images in the transmitted light with NII and N+, x60



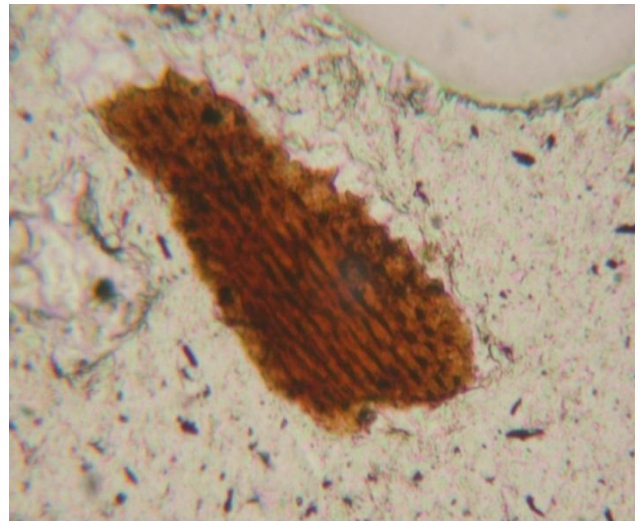
NII: garnet, biotite (limonitized), plagioclase and quartz



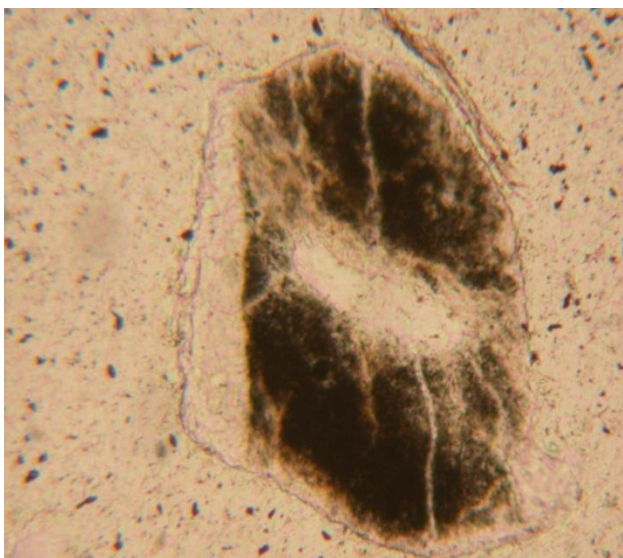
N+: plagioclase with polysynthetic twins



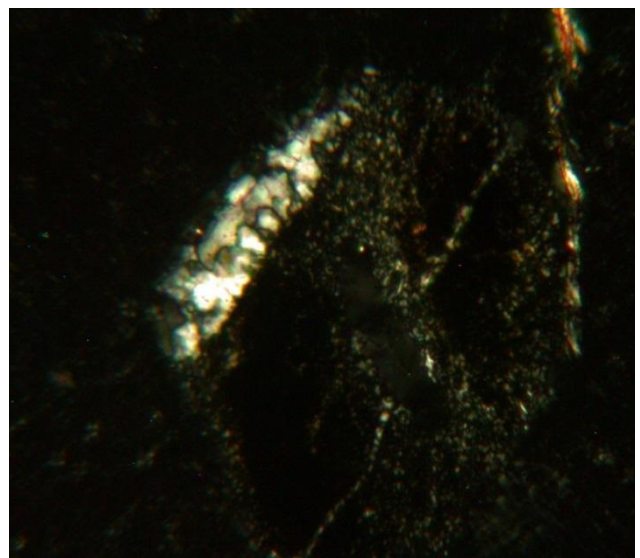
NII: twinned amphibole (actinolite)



NII: limonitized biotite with schlieren of ilmenite



NII: clast of quartz invaded by coally material

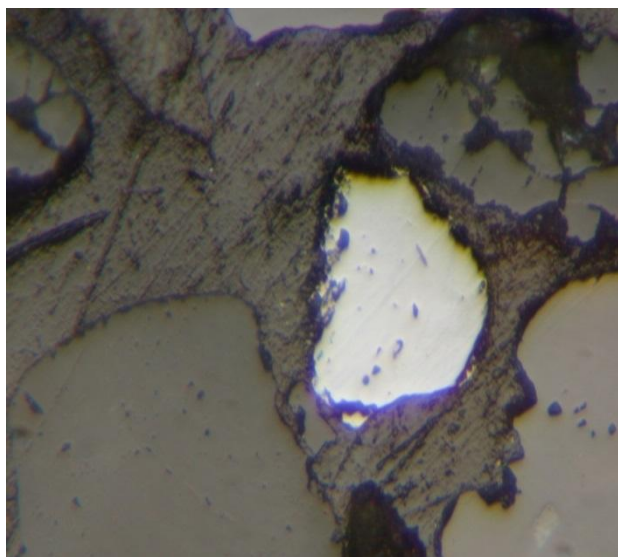


The same view, with crossed nicols; Remarkable is the polygranular character of the quartz clast

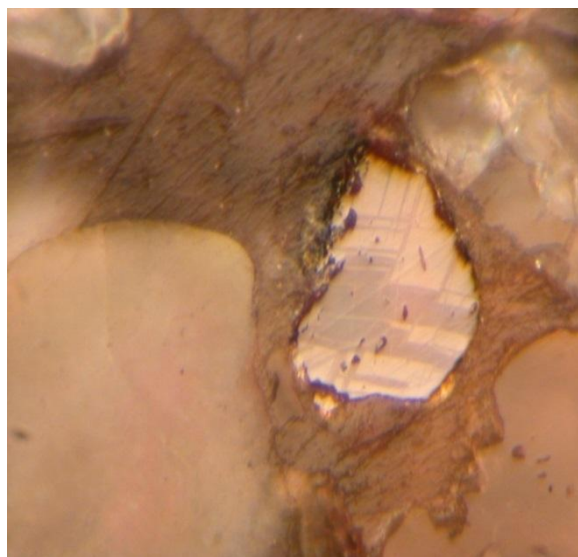


### PLATE III

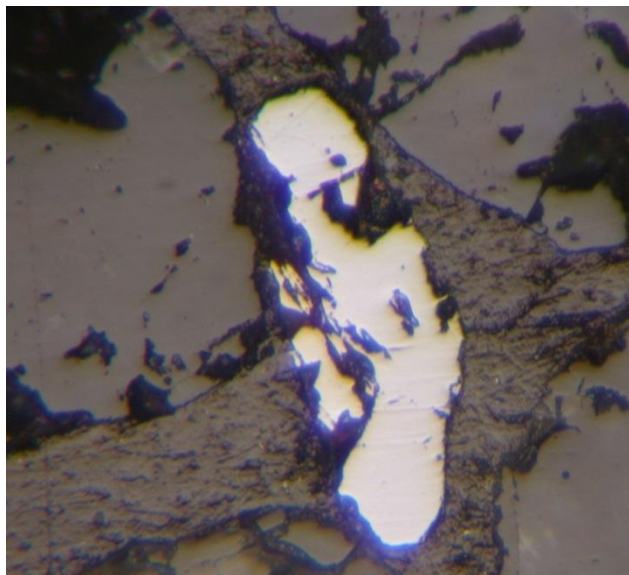
Images in reflected light with 40x



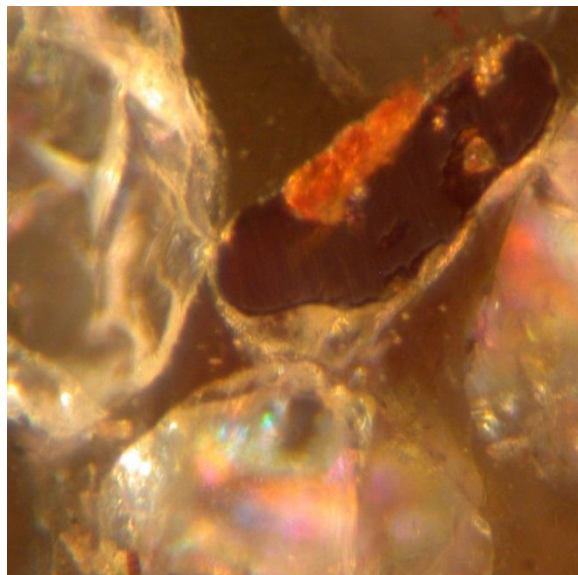
NII: granoclast of ilmenite associated with quartz



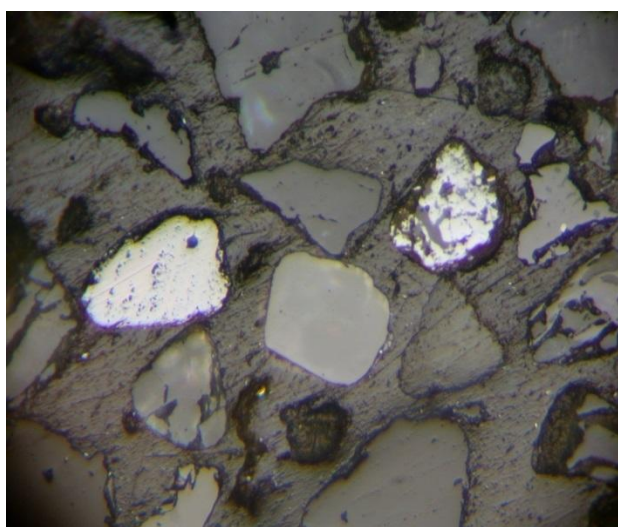
Same view with N+



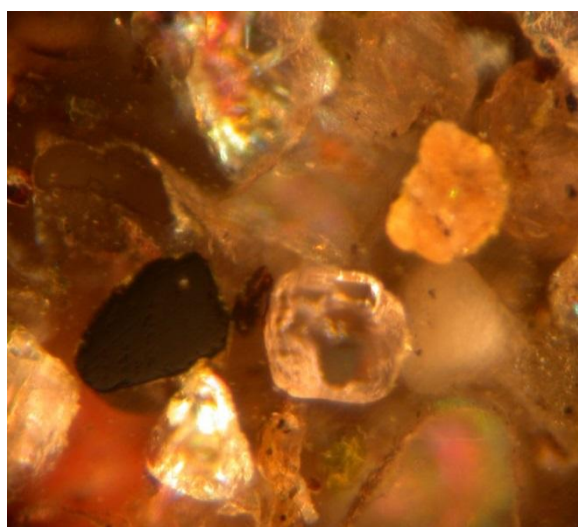
NII: granoclast of ilmenite and rutile



Same view with N+



NII: granoclast of magnetite (left) and goethite



Same view with N+

## GEOCHEMISTRY OF TITANIUM HEAVY MINERALS IN STREAM SEDIMENTS FROM THE BISTRIȚA AURIE RIVER (ROMANIA)

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**Abstract:** The present study focuses on the titanium heavy minerals sampled from alluvial sediments of the Bistrița Aurie River, in order to determine the provenance and the potential economic value, using their geochemical characteristics. A number of 8 selected samples have been collected and separated by gravity concentration in a gold pan. The resulted alluvial concentrates were mounted in thin sections. Identification of the titanium minerals has been carried out by using SEM-EDX analysis. Therefore, the mineral species founded in the alluvial concentrates are: ilmenite (most abundant), rutile, leucoxene, titanite and titano-magnetite. The source of the ilmenite grains is represented by the medium grade metamorphic rocks of Rebra and Bretila Metamorphic Units, while the source of rutile grains is represented by the low-grade metamorphic rocks of the Tulgheș Metamorphic Unit. The average TiO<sub>2</sub> content, greater than 50 wt. % for more than 90 % of the titanium minerals from the Bistrița Aurie River sediments, increases the potential economic value of the Bistrița Aurie alluvial sediments.

**Keywords:** titanium minerals, Bistrița Aurie, alluvial sediments, provenance, potential economic

### INTRODUCTION

The investigated river sediments derived from the exposed volcanic, metamorphic and sedimentary rocks of the Bistrița Aurie hydrographic basin. In addition to the major constituents of the alluvial sediments (quartz, feldspars, and lithic fragments), they contain small quantities of other mineral grains, including heavy minerals (Joshua and Oyebanjo, 2009), defined as minerals having a higher density than quartz, 2.65 g/cm<sup>3</sup>, or densities greater than 2.85 g/cm<sup>3</sup> (Elsner, 2010). The heavy minerals from the river sediments have been studied for the determination of economic potential regarding the presence of gems (Perera et al, 2013), gold and other strategic minerals such as zircon, ilmenite, rutile, monazite etc. (Surour et al, 2003; Dill, 2008; Elsner, 2010). Another approach for the heavy minerals research is the study of morphology (Moral Cardona et al., 2005; Dill, 2007) and grain size (Joshua and Oyebanjo, 2010) but most of the investigations are related to petrogenetic and provenance studies.

The current research focused on the presence of titanium oxides as heavy minerals in alluvial sediments of the Bistrița Aurie River. The chemistry of individual grains has been used in order to trace and characterize the source rocks. Other issues discussed here, refer to the identification and composition of titanium oxides in order to show their possible economic significance.

### GEOLOGICAL FRAMEWORK

The Bistrița Aurie River springs from Rodna Mountains and ends on the confluence with Dorna River. It has a length of about 70 km, 19 tributaries on the right side and 19 on the left side, and crosses localities as Cărlibaba, Ciocănești, Iacobeni and Vatra Dornei (Donisă and Poghirc, 1968). The age of the Bistrița valley is Pliocene-Quaternary (Donisă, 1968).

On the Bistrița Aurie drainage basin outcrops medium and low-grade metamorphic rocks belonging to Crystalline-Mesozoic Zone (CMZ) of the Eastern Carpathians (Fig. 1). The CMZ belongs to the eastern Getides found in the crystalline basement of the Transylvanian Basin. It consists of several Alpine tectonic units with eastern vergency, sheared in Austrian tectogenesis (Albian) (Balintoni, 1997; Hârtopan, 2004). From top to bottom, these are: Bucovinian, Subbucovinian and Infrabucovinian nappes (Săndulescu, 1984). Regarding the description of the metamorphic sequences in the CMZ, Bretila, Tulgheș, Negrișoara, Rebra and Rodna Metamorphic Units are individualized (Balintoni, 2005). Occasionally, Triassic conglomerates, sandstones, limestones, dolomites and lamprophyres veins that penetrate the crystalline rocks appear (Podașcă, 2000; Săndulescu, 1984).

The Rebra Unit, a medium-grade sequence, is a typical continental margin sedimentary pile that contains micaschists interbedded with limestones and amphibolites. The Bretila Unit is also a medium grade sequence dominated by gneissic and amphibolitic rocks. Instead, the Tulgheș Metamorphic Unit is a low-grade sequence (Dill et al., 2012).

### ANALYTICAL METHODS

A number of 8 selected samples shown in Fig. 1 have been collected from the meanders, inside the bend deposition, from the gravel bars and from the alluvial cones. After they were sieved through a 2 mm

mesh, the samples were separated by gravity concentration in a gold pan (according to Silva, 1986). This procedure has been followed by removing the ferromagnetic fraction with a magnet bar. The alluvial concentrates were mounted in Epidian epoxy resin, polished and coated with carbon. The identification of the titanium oxides was done by using a VEGA II LSH SEM with EDX system type QUANTAX QX2 (analytical conditions: accelerating voltage 30 kV), from Interdisciplinary Platform Laboratory of Scientific Investigation and Cultural Heritage Conservation - ARHEOINVEST, from the "Al. I. Cuza" University of Iași. Hence, the mineral classification is purely based on the chemical composition of the measured grains. The distinction between ilmenite, leucoxene and rutile is based on the  $\text{TiO}_2$  wt. % content only: 21 wt. %  $\text{TiO}_2$  < Ti-magnetite < 46 wt. %  $\text{TiO}_2$  < ilmenite < 70 wt. %  $\text{TiO}_2$  < leucoxene < 87.5 wt. %  $\text{TiO}_2$  < rutile (Keulen et al., 2012). Therefore, the  $\text{TiO}_2$  polymorphs (i.e., rutile, anatase and brookite) cannot be distinguished in all the cases and are grouped as one mineral species.

## RESULTS AND DISCUSSIONS

The principal sources of Ti, used on a large-scale in industry, are the following minerals: ilmenite, leucoxene, and rutile (Keulen et al., 2012). One of the most essential parameter to the assessment of quality and economics of a potential deposit is the determination of the  $\text{TiO}_2$  average content of the Ti minerals (Elsner, 2010).

The titanium oxides have been described in all the analyzed samples both as individual grains and as inclusions in others heavy minerals species. So, the titanium mineral species founded in the alluvial concentrates are: rutile, ilmenite, leucoxene, titanite and titano-magnetite. Ilmenite is the most abundant titanium mineral. About 40% of ilmenite crystals have a concentration very close or identical to the ideal stoichiometric value of 52.6 wt. % (Fig. 2).

When the concentration of  $\text{TiO}_2$  is more than 60 wt. % it will denote a continuous alteration of primary ilmenite. This alteration via pseudorutile to leucoxene is attributed to complex processes of oxidation and hydroxylation associated with leaching of Fe, leading to a significant increase in the  $\text{TiO}_2$  grade of the Ti mineral fraction (Grey and Reid, 1975; Keulen et al., 2012; Babu et al., 2013). Also, a very sensitive proxy for the sediment maturity is the average  $\text{TiO}_2$  content of the ilmenite fraction (Grey and Reid, 1975; Keulen et al., 2012).

In this study, the average  $\text{TiO}_2$  content, greater than 50 wt. % for more than 90 % of the Ti minerals from the Bistrița Aurie River sediments (Fig. 2), as one of the most essential parameter to the assessment of quality and economics of a potential deposit, indicate progressive leaching of Fe from primary ilmenite specifically to mature sediments. This fact increases the potential economic value of the Bistrița Aurie alluvial sediments.

By studying only the  $\text{TiO}_2$  content is very hard to define the source of the detrital ilmenite. Nevertheless, titanium minerals occur in all the samples together with garnets (Almandine 80-100 %). Ilmenite is described very often as inclusion in garnet (Fig. 3A) or staurolite (Fig. 3B), together with quartz, apatite and zircon. Thus, its source can be attributed to the medium-grade metamorphic rocks belonging to Rebra and Bretila Metamorphic Units.

The rutile crystals that occur in alluvial concentrates show very often a sagenitic structure that forms a network of equilateral triangles or rhomboids. Marginal rutile crystals are smaller and less frequent (Fig. 3C). The remaining free space is occupied by hematite (Fig. 3C, D) and chlorite after biotite. Such aggregates are described by Balintoni and Chițimuş (1973) as a rutile paramorph after brookite, in the Tulgheș Metamorphic Unit. These paramorphs are attributed to the initial metamorphosis of Tulgheș unit, and the transformation of biotite to chlorite is hercynian and corresponds to last retrograde metamorphic event (Balintoni and Chițimuş 1973). The titano-magnetite occurs very rare in the alluvial concentrates because of the pretreatment related by removal of ferromagnetic fraction. The titanite occurs only as inclusions in garnet.

## CONCLUSIONS

The titanium mineral species found in the alluvial concentrates are: ilmenite (the most abundant), rutile, leucoxene, titanite and titano-magnetite. The average  $\text{TiO}_2$  content, greater than 50 wt. % for more than 90 % of the Ti minerals from the Bistrița Aurie River sediments is specific to mature sediments. This fact increases the potential economic value of the analyzed alluvial sediments. The ilmenite grains originated most probably in the medium grade metamorphic rocks belonging to Rebra and Bretila Metamorphic Units.

On the other hand, the source of rutile grains is the low grade metamorphic rocks of the Tulgheș Metamorphic Unit.



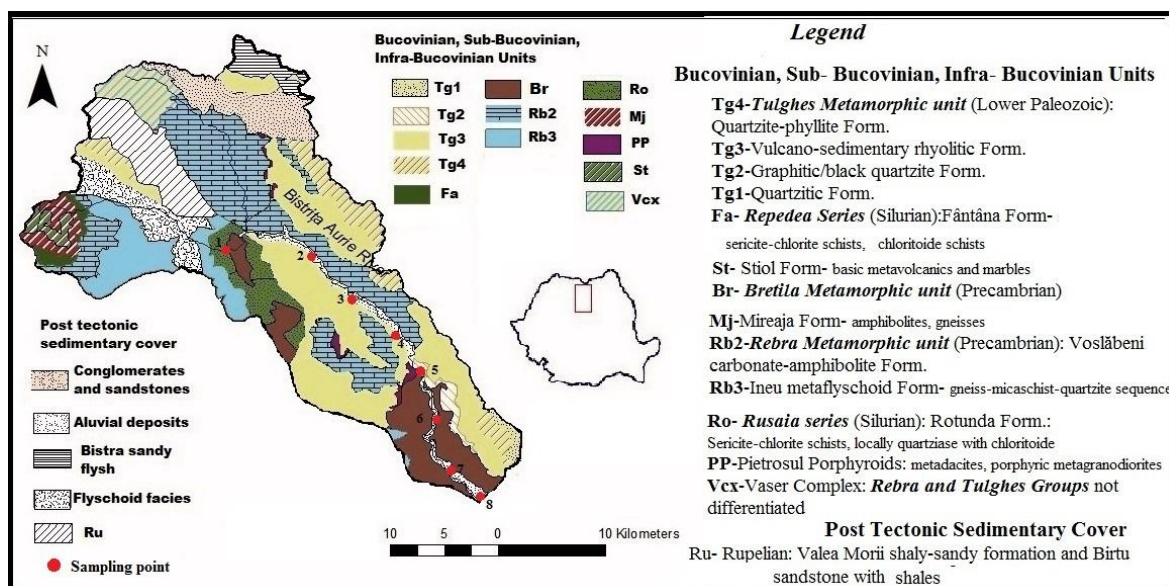


Fig. 1 Geological Map of the Bistrița River drainage basin (modified after Krautner and Bindea, 2000; scale 1:200000), showing the sample location.

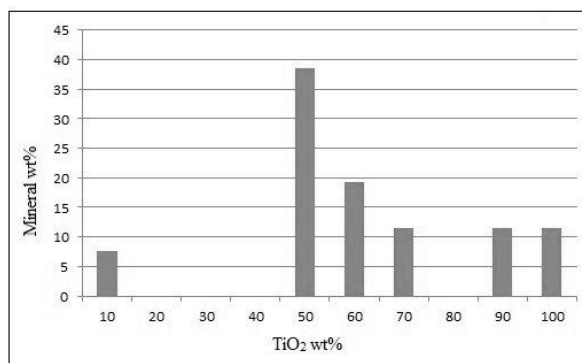


Fig. 2 Average TiO<sub>2</sub> content of the Ti mineral fraction in Bistrița Aurie River sediments.

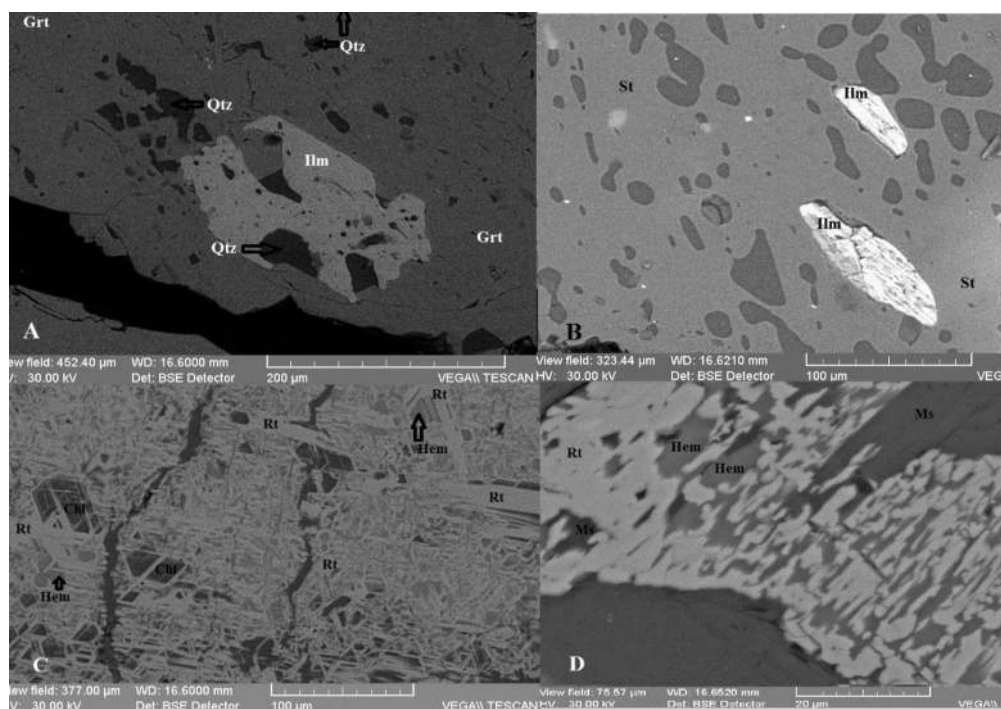


Fig. 3. A - BSE image of a detrital garnet with ilmenite and quartz inclusions; B - BSE image of a detrital staurolite with ilmenite inclusions (inclusions of poikilitic quartz can be seen); C - BSE image of a rutile with sagenitic structure; D - BSE image of a rutile detrital mineral.

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## PRELIMINARY DATA ON THE GEOCHEMISTRY OF THE STRĂJII VALLEY TAILING POND (SUCEAVA COUNTY, ROMANIA)

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**Abstract.** Specific characteristics and some mineralogical and geochemical aspects of the mine tailings derived from the ore processing plant of Tarnița represent a potential risk for the environment. The material of the tailing pond mostly has a greyish color, rarely a yellow-ochre one, and consists mainly of fine and very fine sand, silt and clay fractions (more than 75%). In terms of the mineralogy, the primary minerals have been identified as quartz, sericite, chlorite, pyrite, subordinate sphalerite, galena and accidentally barite; secondary minerals (probably sulfates) have been recognized as well. The rate of soluble fraction has a relative wide range, from 3.78 to 34.71%, the average abundance being of 11.15%; the values of leaching solution pH are extremely low (from 2.46 to 2.89), with an average of 2.67. Chemical analysis showed that the concentrations are very high for both toxic elements (Pb>As>Cr>Co) and major elements (Fe>Al>Mg>Mn). In this occurrence the relationships between the elements, as well as that of the elements with the soluble fraction, showed some significant correlations, as follow: soluble fraction with Mg > Al > As > Pb > Mn; Al with Mg > Mn; Mg with Pb > As; Pb with As; Fe only with Co. Cr displays no correlation.

**Keywords:** mine tailing, mineralogy, geochemistry, XRF, acid mine drainage, toxic metals.

### 1. Introduction

The present preliminary study focuses on the description of the mine tailings resulted from the ore processing plant of Tarnița. The Tarnița ore processing plant operated from the 1950s to 2007, and had two units of extraction (through flotation processes): the extraction of Cu from the Cu-rich pyrite and the unit aimed to benefit barite extraction; both of them produced large amounts of waste material, deposited on large areas near the processing plant.

The tailing pond under study is located nearby the Puzdra county road 177A (Holda - Frasin) on the territory of Ostra village, at about 6 km SW from its center; more exactly, the waste deposit is on the Valea Străjii valley, at a distance of about 800 m from the Suha River. It has an elongate shape (as a cone), with a length of roughly 500 m; the maximum width is of 250 m at its northwestern sector, where an unconsolidated dump is built (Fig. 1). In the SE part of the tailing pond (in the peak of the cone), a pool of water was accumulated. The material of the tailing pond generally has a greyish color, but in some places it displays a yellow-ochre tint; it contains non-aggregated minerals, in other words it has a sandy appearance.

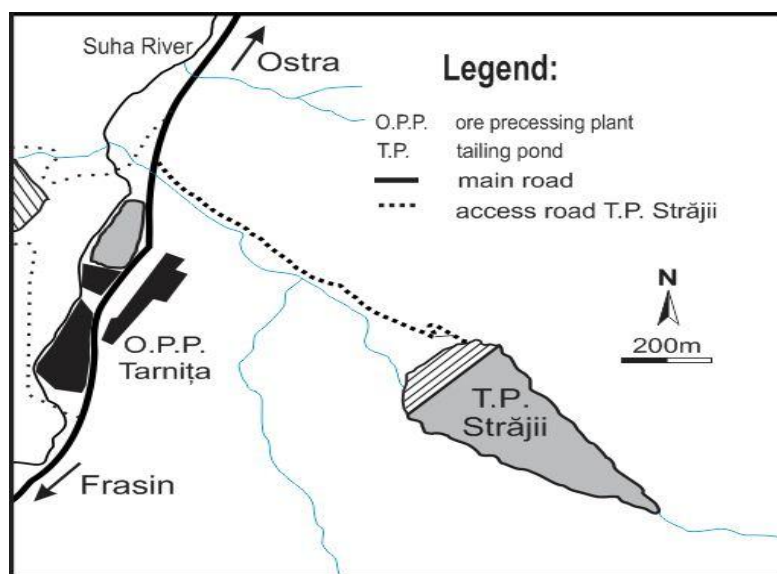


Fig. 1. The location of the tailing pond from Străjii Valley.

## 2. Geological setting

The Cu-rich polymetallic belt developed along the Eastern Carpathian, with a length of about 200 km, being associated to the low-grade metamorphic schists of the Tulgheș Group (Lithogroup – Balintoni, 1997), which consists mostly of quartz-schists, sericite-schists and chlorite-schists (Kräutner, 1980). The Tulgheș group has been divided in five lithostratigraphic formations, namely Tg1-Tg5 (Kräutner, 1980), or in four lithostratigraphic units by other authors, who named them lithozones (Balintoni, 1997). The sulfide mineralizations are associated to the Tg3 unit, which approximately corresponds to the Leșu Ursului lithozone.

The polymetallic ores were concentrated in three metallogenic districts, as follow (from NNW to SSE): (1) Borșa-Vișeu; (2) Fundu Moldovei-Leșu Ursului; and (3) Bălan-Fagu Cetății (Kräutner, 1980). The Leșu Ursului metallogenic field is part of Fundu Moldovei – Leșu Ursului District and lies roughly in the center of the Polymetallic Belt. In the metallogenic field of Leșu Ursului the mineralizations are of fine-grain polymetallic type and consist of pyrite, chalcopyrite, sphalerite, and galena; low amounts of arsenopyrite, pyrrhotite, tetrahedrite and bournonite occur as well (Kräutner, 1980). At Ostra, barite and witherite are associated with base metal ores. The barite veins cut the metamorphic basement and Mesozoic sedimentary cover.

## 3. Materials and methods

The mineralogy of the waste was determined using a Stereo Optika SZM2 stereo microscope, with a magnification of up to 45×; part of the samples were washed with distilled water, in order to have more accurate images of the primary mineral grains. The grain size of the samples was determined using the dry sieving method; four fractions were identified, as follow: > 1 mm; 1 – 0.25 mm; 0.25 – 0.063 mm; < 0.063 mm. The analysis of pH was performed based on leaching tests (1:5 solid/liquid ratio), at the room temperature, with a MeterLab PHM 250 Ion Analyzer – Corning 555. Also, the soluble fraction was determined, by adapting the gravimetric method for total filterable solids.

The chemical analyses for both major elements and toxic elements (Al, Fe, Mg, Mn, Cr, Co, Pb, and As) were carried out through the XRF spectrometry, using an ED-XRF Epsilon 5 spectrometer.

## 4. Results and discussions

The grain-size distribution of the material from the tailing pond is shown in Figure 2. The grain size distribution analyses reveal extremely large variation in the following four grain size classes: 0 – 31.20 % grains similar to very coarse sand (>1.0 mm); 2.04 – 40.16 % grain similar to coarse and medium sand (1.0–0.25 mm); 25.16 – 79.06 % grain similar the fine and very fine sand (0.25– 0.063 mm); and 4.22 – 43.30 % - similar to silt and clay fraction (< 0.063 mm). The mean values of the recorded data denote that the largest mass of the tailing consists of fine and very fine sand-size particles (average higher than 55 %) and silt + clay (average higher than 20%).

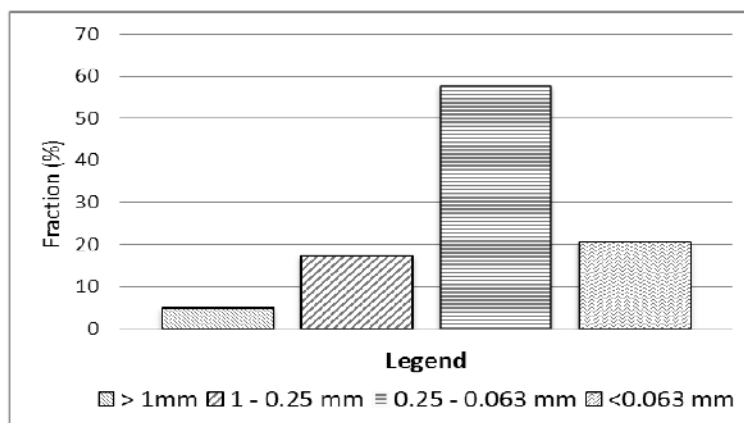


Fig. 2. Grain-size distribution of the investigated mine tailings.

The physical parameters of the waste materials increase the environmental risk of the mine tailing, because the small particles can be carried out toward the environment either through mechanical transport during rainfall events or by wind-borne transport (Stumbea and Chicoș, 2012; Quispe et. al., 2013).

Microscopical investigation showed that the material is formed mainly of quartz, sericite, and pyrite; subordinate chlorite, sphalerite, galena and accidentally barite were observed. The samples with greyish

color are more abundant in galena; the next most-abundant mineral is quartz, then sericite. In terms of the yellow-ochre samples, quartz is more abundant and it is highly limonitized. Also, the presence of some aggregates on the surface of the primary minerals (e.g. quartz, pyrite) has been noticed. According to previous researches, these aggregates consist of hydrated sulfates of Al, Fe, Mg, Mn and incorporate toxic elements in their structures (Moncur et al., 2005; Hammarstrom, et. al., 2005). This is in agreement with Stumbea's results (unpublished data) that identified within the waste of an another tailings pond from the same perimeter, the presence of jarosite, alunogen, copiapite, and coquimbite. The sulfates developed within the waste material of the mine tailing are generally very soluble and they are an important factor that generate acidity and high concentrations in toxic elements, SO<sub>4</sub> and Fe (Blowes et al., 2005; Carbone et. al., 2013).

In this preliminary paper, the abundance of the soluble fraction from the mine tailings was also determined. The soluble fraction ranges within a relative wide interval, from 3.78 to 34.71 %, with an average of 11.15%. Regarding the acidity of the material from the tailing pond, the analyses showed a very low pH (< 3), with a range between 2.46 and 2.89, and an average of 2.67.

The statistical summary of the chemical composition of the tailing samples, in terms of major elements (Al, Fe, Mg and Mn) and toxic elements (Cr, Co, Pb and As), is presented in Table 1, where minimum, maximum and average data are indicated for each element.

**Table 1.** The statistical summary of the amount of primary elements (Al, Fe, Mg, and Mn) and toxic elements (Cr, Co, Pb and As) (*n*= 23)

	<b>Al</b> <b>(wt %)</b>	<b>Fe</b> <b>(wt %)</b>	<b>Mg</b> <b>(wt %)</b>	<b>Mn</b> <b>(wt %)</b>	<b>Cr</b> <b>(ppm)</b>	<b>Co</b> <b>(ppm)</b>	<b>Pb</b> <b>(ppm)</b>	<b>As</b> <b>(ppm)</b>
Minimum	3.27	9.44	0.05	0.01	11.00	24.80	219.00	64.50
Maximum	16.71	18.43	3.15	0.02	92.00	52.80	4073.00	326.40
Average	8.41	12.46	1.27	0.02	35.91	32.50	1412.78	139.00

Concerning the concentrations presented in the Table 1, a wide ranges of data can be observed. Moreover, the average values for all samples exhibit very high concentrations of toxic elements (Pb, As, Cr, and Co) and some major elements (Al, Fe and Mg), except for Mn which shows a roughly low amount. The highest concentration among the determined toxic elements is shown by Pb (an average of 1413 ppm) and As (an average of 139 ppm). The waste material of the mine tailing is a source of contaminants with high concentrations in toxic elements, high acidity and probably SO<sub>4</sub> and Fe from the very soluble sulfates. The chemical analyses show the following concentration ratios, in a decreasing order of abundance: Pb>As>Cr>Co (toxic elements) and Fe>Al>Mg>Mn (major elements).

In order to establish the relationships between the elements considered in this study, a Pearson correlation matrix has been calculated (Table 2). Thereby, Pb and As have a positive correlation with some major elements (Al, Mn, Mg). In addition, the above mentioned toxic elements – on one hand, and the major elements – on the other, revealed correlations between them. Moreover, all these elements show correlations with the soluble fraction. Fe concentration only correlates with Co, and both display no correlation with the soluble fraction. However, it is important to note that some of them (e.g., Cr) displays no correlation with either other elements or soluble fraction.

**Table 2.** Pearson's correlation matrix between soluble fraction, primary elements and toxic elements (*n* = 23)

<b>Variables</b>	<b>Al</b>	<b>Fe</b>	<b>Mg</b>	<b>Mn</b>	<b>Cr</b>	<b>Co</b>	<b>Pb</b>	<b>As</b>	<b>S.F.</b>
<b>Al</b>	<b>1</b>								
<b>Fe</b>	-0.263	<b>1</b>							
<b>Mg</b>	<b>0.903</b>	-0.252	<b>1</b>						
<b>Mn</b>	<b>0.494</b>	-0.236	0.378	<b>1</b>					
<b>Cr</b>	-0.223	-0.206	-0.147	0.348	<b>1</b>				
<b>Co</b>	-0.380	<b>0.975</b>	-0.399	-0.310	-0.204	<b>1</b>			
<b>Pb</b>	<b>0.660</b>	-0.005	<b>0.704</b>	0.390	-0.158	-0.149	<b>1</b>		
<b>As</b>	<b>0.611</b>	0.168	<b>0.639</b>	0.392	-0.190	0.045	<b>0.938</b>	<b>1</b>	
<b>S.F.</b>	<b>0.767</b>	-0.020	<b>0.789</b>	<b>0.555</b>	-0.173	-0.169	<b>0.649</b>	<b>0.681</b>	<b>1</b>

S.F. = soluble fraction; values with correlation are in bold.

These findings, associated with those mentioned above (the identified mineral aggregates, high abundance of soluble fraction, high acidity, high concentrations in toxic elements and major elements), lead to the assumption that the studied materials contains sulfates as well. This assumption needs to be proved by further studies based on X-ray diffractometry.

## 5. Conclusions

This study presents some geochemical aspects regarding the materials of the tailing pond from the Străjii Valley, resulted from the flotation plant of Târnița. In terms of mineralogy, the identified sulfide minerals are pyrite and subordinate sphalerite and galena. Gangue is not very variable, being mainly composed of quartz and sericite; accidentally, chlorite and barite were observed as well. The largest mass of the tailing consists of fine and very fine sand-size particles; the silt and clay fractions are also well represented. The amount of the soluble fraction ranges within a relative wide interval (3.78-34.71%) and the leaching solutions exhibit a very low pH (2.46 - 2.89). The concentrations in major and toxic elements are very high. Thus, Fe and Al have a very high concentration with means of 12.46% and 8.41%, respectively. A relatively high concentration is shown by Mg (mean of 1.23 %), while Mn has a roughly low concentration, with a mean of 0.02%. In terms of the mean amount of the toxic elements, the following sequence of abundance has been identified: Pb (1413 ppm) > As (139 ppm) > Cr (36 ppm) > Co (32 ppm). A part of the elements are highly correlated between them or with the amount of soluble fraction, a fact that might be explained by the presence of the sulfates within the waste material. This study underlined once again the potential risk of the mine tailing for the environment.

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## DETERMINATION OF PHOSPHOGYPSUM FROM ROMANIA BY SEM-EDAX

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### Abstract:

Phosphogypsum is a technogenic product remaining after the extraction of phosphoric acid from raw phosphate, mainly apatite. The phosphate rock mainly composed of apatite, and originating from Morocco, Russia, Syria, Jordan and India, is treated with concentrated sulfuric acid (96%), after fine crushing to supra colloidal size and passing into an aqueous solution of phosphoric acid.

The morphology of crystals is influenced by the conditions of phosphoric acid manufacture. Most of the analyzed crystalline phases, especially gypsum, have micronic size, are very water absorbing and are detectable only at the level of crystalline individual through the scanning electron microscopy.

**Keywords:** deposits, phosphogypsum, SEM, phosphates, EDAX

### 1) Introduction:

Phosphogypsum from three deposits in Romania, i.e. Turnu Măgurele, Năvodari and Bacău, made the object of our study. The total area of these deposits is of 182.5 ha, and the total quantity of phosphogypsum is 18.106 t. The phosphogypsum was formed as a result of environmental factors. A macroscopic study of the phosphogypsum was carried out, revealing a powdery or sandy appearance. At the surface it has a relatively harsh crust. The color is white-yellow or ginger. The presence of brushite, as a second phases of phosphogypsum was mentioned by Caravețanu (2013).

Direct observations on the samples, argued that phosphogypsum from the three deposits are very similar at first sight. However, at this point, we observed some minor differences.

Four morphological types can be separated according to their appearance (Fig.1):

- 1) phosphogypsum with sandy appearance and yellow color (Fig. 1.A);
- 2) phosphogypsum as crusts (Fig. 1.B - some granules of white color can be noticed within it);
- 3) phosphogypsum with powdery appearance and yellow color (Fig. 1.C);
- 4) nacreous and white phosphogypsum (Fig. 1.D - the broken pieces in the picture were collected for analyses).

The minerals present micronic size and the crystals are detectable only by scanning electron microscopy.

### 2) Methods:

10 samples of phosphogypsum from Năvodari, 10 samples of phosphogypsum from Turnu Măgurele and 5 samples of the Bacău phosphogypsum have been analyzed by using the scanning electron microscopy. The samples were coated with QUARUM Q150 R ES, or gold.

The scanning electron microscopy was performed with a „JEOL JSM 6400 SCANNING MICROSCOPE”. The accelerating voltage was 15KV.

The semi-quantitative determination of the composition was determined by using EDAX method on the points marked on the SEM images in Fig. 2.

### 3) Results:

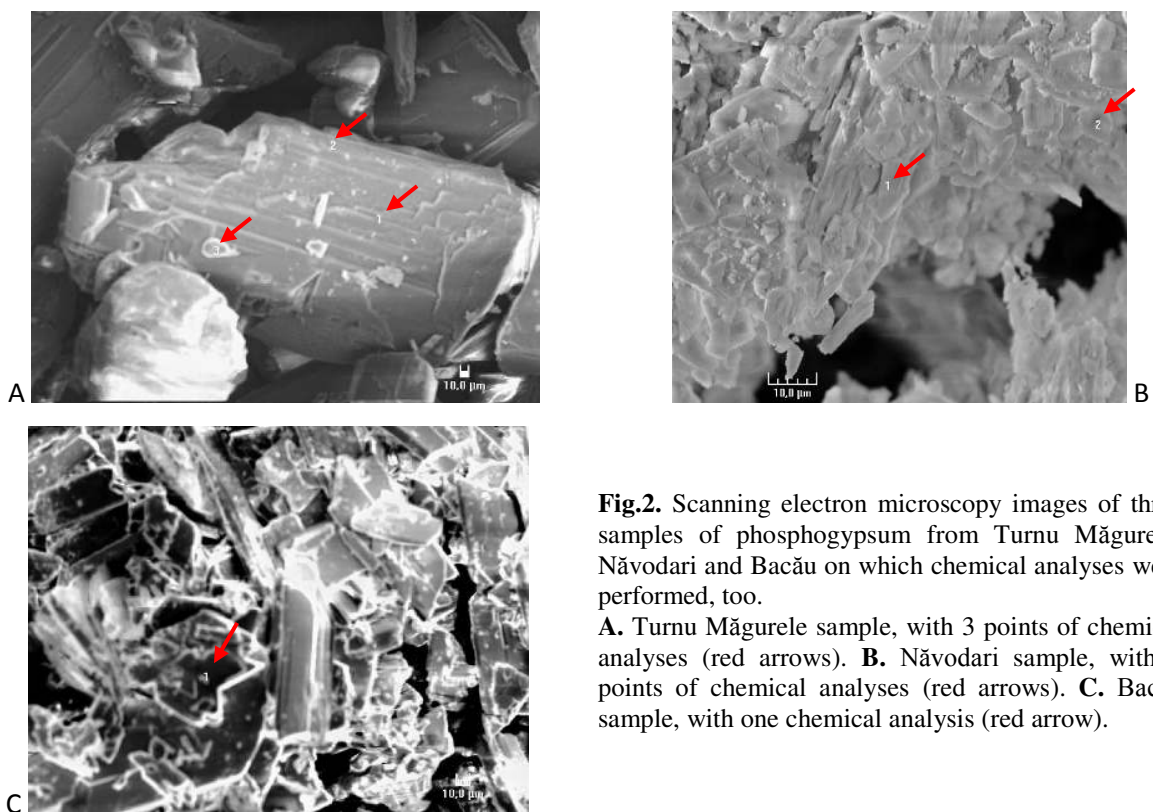
As it can be seen in Fig. 2.A, B and C, the phosphogypsum predominates in the samples.

This composition (At%) is presented in Table 1. The data obtained from EDAX analyses have been plotted in ternary diagrams (Fig. 3). From Table 1 and Fig. 3, it can be noticed that SO<sub>4</sub> predominates and PO<sub>4</sub> is in small quantities in the analysed samples.





**Fig.1.** Representatives images of Romanian phosphogypsum from Turnu Măgurele (A and D), Năvodari (B), and Bacău (C).



**Fig.2.** Scanning electron microscopy images of three samples of phosphogypsum from Turnu Măgurele, Năvodari and Bacău on which chemical analyses were performed, too.

**A.** Turnu Măgurele sample, with 3 points of chemical analyses (red arrows). **B.** Năvodari sample, with 2 points of chemical analyses (red arrows). **C.** Bacău sample, with one chemical analysis (red arrow).



Table 1. The data obtained from EDAX analyses for the phosphogypsum samples from Romania.

Turnu Măgurele	At%			Năvodari	At%			Bacău	At%		
	(SO <sub>4</sub> ) <sup>2-</sup>	Ca	(PO <sub>4</sub> ) <sup>3-</sup>		(SO <sub>4</sub> ) <sup>2-</sup>	Ca	(PO <sub>4</sub> ) <sup>3-</sup>		(SO <sub>4</sub> ) <sup>2-</sup>	Ca	(PO <sub>4</sub> ) <sup>3-</sup>
1	39.40	58.36	1.50	1	39.40	58.36	1.50	1	53.62	42.34	2.07
2	52.19	46.91	0.91	2	52.19	46.91	0.91	2	39.55	56.62	3.10
3	33.97	62.77	2.55	3	33.97	62.77	2.55	3	25.88	72.00	1.09
4	45.90	51.93	1.87	4	45.90	51.93	1.87	4	51.88	46.88	1.21
5	24.74	66.20	7.21	5	24.74	66.20	7.21	5	51.76	47.46	0.77
6	0.38	1.07	0.11	6	0.38	1.07	0.11	-	-	-	-
7	0.38	1.07	0.11	7	0.38	1.07	0.11	-	-	-	-
8	40.72	57.35	1.84	8	40.72	57.35	1.84	-	-	-	-
9	49.03	48.71	1.94	9	49.03	48.71	1.94	-	-	-	-
10	49.61	48.33	1.75	10	49.61	48.33	1.75	-	-	-	-
11	51.33	46.67	1.71	11	51.33	46.67	1.71	-	-	-	-
12	52.10	46.32	1.46	12	52.10	46.32	1.46	-	-	-	-
13	46.65	52.51	0.84	13	46.65	52.51	0.84	-	-	-	-
14	47.64	48.63	3.37	14	47.64	48.63	3.37	-	-	-	-
15	52.63	45.33	1.64	15	52.63	45.33	1.64	-	-	-	-
16	53.21	46.68	1.91	16	53.21	46.68	1.91	-	-	-	-
17	46.81	51.19	1.48	17	46.81	51.19	1.48	-	-	-	-
18	2.02	51.18	43.79	18	2.02	51.18	43.79	-	-	-	-
19	53.22	43.75	2.59	-	-	-	-	-	-	-	-
20	54.14	43.78	1.75	-	-	-	-	-	-	-	-
21	51.62	46.01	2.15	-	-	-	-	-	-	-	-
22	54.75	42.98	2.17	-	-	-	-	-	-	-	-
23	53.10	43.92	2.03	-	-	-	-	-	-	-	-
24	53.94	44.20	1.72	-	-	-	-	-	-	-	-
25	54.46	43.27	2.15	-	-	-	-	-	-	-	-
26	54.61	43.14	1.93	-	-	-	-	-	-	-	-
27	52.70	43.91	2.40	-	-	-	-	-	-	-	-
28	54.42	45.00	0.58	-	-	-	-	-	-	-	-
29	48.91	50.06	1.02	-	-	-	-	-	-	-	-
30	54.24	42.74	2.37	-	-	-	-	-	-	-	-
31	53.89	44.64	1.39	-	-	-	-	-	-	-	-
32	54.29	41.65	3.54	-	-	-	-	-	-	-	-
33	35.15	63.61	1.24	-	-	-	-	-	-	-	-
34	53.81	41.42	4.00	-	-	-	-	-	-	-	-
35	54.27	41.67	3.41	-	-	-	-	-	-	-	-
36	54.11	42.60	3.17	-	-	-	-	-	-	-	-
37	42.48	56.22	1.30	-	-	-	-	-	-	-	-
38	52.62	41.72	4.05	-	-	-	-	-	-	-	-
39	52.42	37.75	3.20	-	-	-	-	-	-	-	-
40	55.25	40.21	3.54	-	-	-	-	-	-	-	-
41	55.07	42.39	2.47	-	-	-	-	-	-	-	-
42	54.86	42.61	2.41	-	-	-	-	-	-	-	-
43	54.29	43.15	1.84	-	-	-	-	-	-	-	-
44	52.42	44.95	2.63	-	-	-	-	-	-	-	-
45	54.11	42.62	2.64	-	-	-	-	-	-	-	-
46	53.59	43.57	2.46	-	-	-	-	-	-	-	-
47	53.96	41.44	3.91	-	-	-	-	-	-	-	-
48	52.78	44.42	2.80	-	-	-	-	-	-	-	-

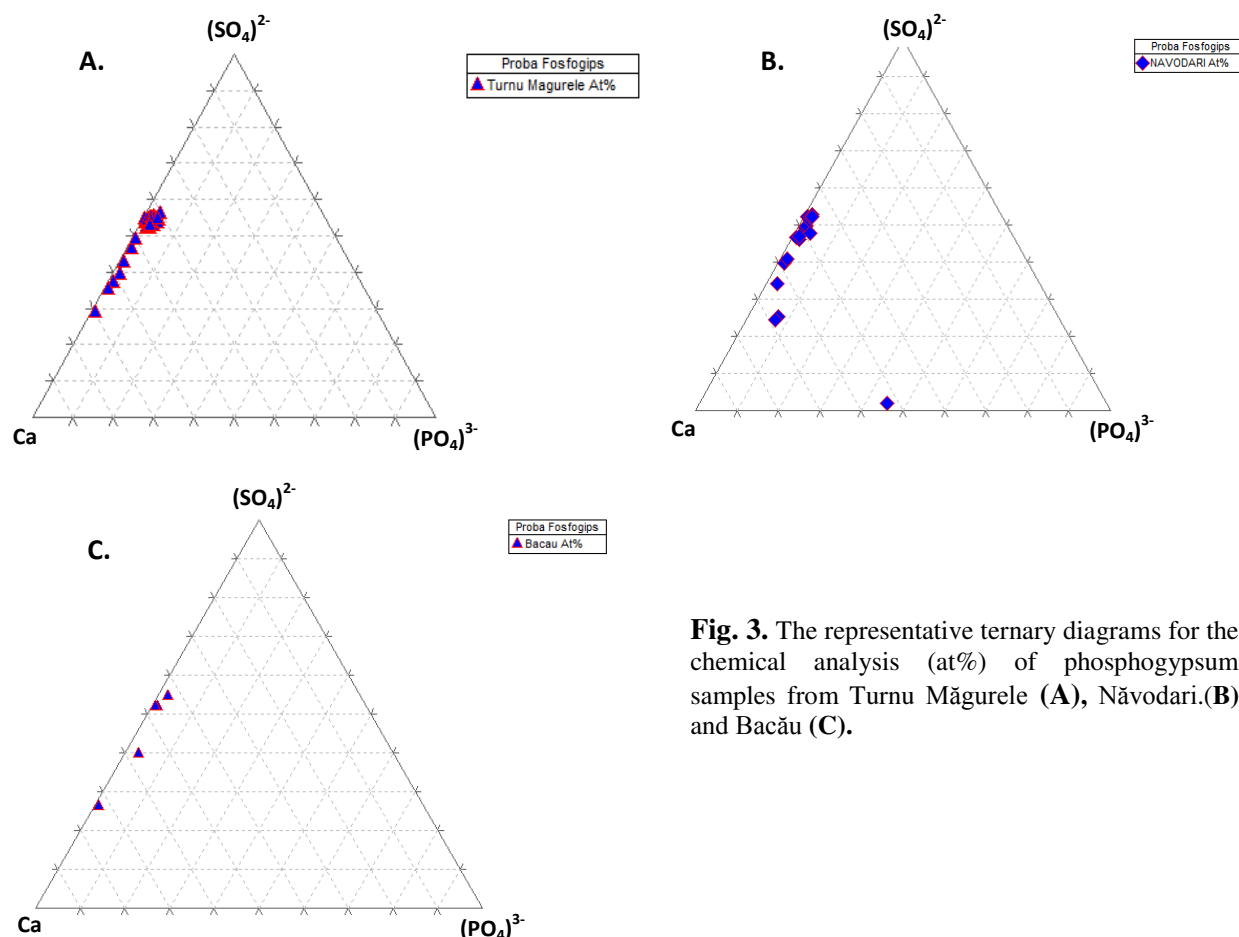
#### 4) Discussion

The gypsum crystals are prismatic to acicular, showing perfect cleavage after [001]. Individual crystals have lengths ranging from 10 to 120  $\mu\text{m}$ . The phosphogypsum crystals of the second morphological type are grouped in polycrystalline, weakly cohesive aggregates. A morphological feature of this type consists of the homogeneous crystal size. Crystal morphology of this group is relatively large and tends to form aggregates of accretion, with randomly oriented and interlocking crystals. The crystal

size varies from 100  $\mu\text{m}$  to 1 mm. The third morphological group of phosphogypsum is dominated by the presence of crystalline aggregates that are similar to the “sand roses”. The largest dimension of the aggregates reaches 1 mm. The fourth morphological group of phosphogypsum is common at the lower levels of all stockpiles and consists of a series of crystalline, cauli-flower-like aggregates. These are practically similar to those of the third group, but the crystalline forms of gypsum are difficult to distinguish.

From the ternary diagram on chemical analyzes of the phosphogypsum samples coming from Năvodari (Fig. 3.B), it results clearly the presence of relict phosphate.

The samples analyzed from Turnu Măgurele and Bacău, suggest a slight substitution with phosphoric acid.



**Fig. 3.** The representative ternary diagrams for the chemical analysis (at%) of phosphogypsum samples from Turnu Măgurele (A), Năvodari.(B) and Bacău (C).

## Conclusion

Scanning electron microscopy was performed on samples collected from the deposits of Turnu Măgurele, Năvodari and Bacău. The analyses resulted in the definition of four morphological types of phosphogypsum. All of the analyzed samples of the first morphological type have compositions close to stoichiometry.

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