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"Mineral Deposits and Environment"

20th - 23rd September 2006, **ALBAC**
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no corrections were made by the editor and the texts have been
printed as received.

The responsibility for the content relies completely on authors.

FOREWORDS

The symposia organized by the Society for Economic Geology of Romania (SEGR) have reached their 5th edition, which marks also 10 years of activity for this non-governmental organization. With each edition, the meetings have raised the most stringent discussion topics of contemporary economic geology; the issues of solid mineral resources, gold, Alpine metallogenesis in the Carpathian structures, etc. For the present edition, a more than actual, some would say "hot" problem, is brought into focus: **the relationship between ore deposits and the environment.**

During the last decades, contemporary (especially economic) geology has been paying increased attention to this particular subject. Its re-emergent character results from the globalization of this problem and, even more so, from an increasing character of **interdisciplinarity**. While some time ago, an exclusive ecological approach has been seen as largely sufficient, now it is more and more approached by physicists, chemists, geologists, geographers, economists, etc., that is, by all research areas involved in the studying of environment or any of its facets. As a consequence, within each of these sciences, an environment-oriented branch emerged, which is also the story of environmental geology.

Environmental geology has individualized as a distinct branch of geology during the 1970s and encompasses the entirety of environmental issues directly linked with geology (earthquakes, volcanism, landslides, mineral resources production and related environmental impacts, etc.). The core element of the last component is that of the mineral resources. The environmental experts perceive the economic need for minerals as a pressure upon society, in direct correlation with the demographic growth and with the whole idea of salvaging the environment. The immediate and pressing effect materializes in a contemporary society becoming ever increasingly demanding with view to the mineral and energetic raw materials resources.

Many of the ongoing projects are being made questionable because of their high risk potential towards the environment and population, and future projects are in their turn suspected to become particularly aggressive factors for the environment. It is for this reason that such projects either came to a standstill or they failed to raise any interest for the investors. From where economic geology stands, this whole atmosphere embodies in a new way to define geological reserves.

The definition of reserves-resources is well known with respect to the three coordinates represented by: geology, economy and feasibility, and which represent the basis for the 3D classification adopted by the UN. This particular way to define and represent

resources must be added with a fourth criterion which may be denominated as the environmental coordinate. The need to introduce this new parameter derives from recognizing a fact which is already applied by all entities involved in the mineral exploration and mining. The requirements and guidelines provisioned by the environmental legislation trigger however, a load of heavier costs for any new exploration project. As a consequence, one may speak about resources in mining areas which may be rehabilitated and returned to some post-operation use, and resources in areas that would turn severely damaged, with no method known to date to allow for environmental remediation. Such resources remain on the stand-by and cannot be extracted.

The topics approached by the present SEGR Symposium "Ore Deposits and the Environment" are in consonance with these new environmental requirements the mining industry has to comply with.

A first due remark concerns the wide variety of papers, ranging from general theoretic issues to applicative approaches regarding environmental protection in ore or coal mining, as well as in oil extraction industry. A particular feature is given by works dealing with environmental issues related to water resources. While papers dealing directly with ore deposits are fewer, they still manage to approach actual problems of gold and non-ferrous ore metallogeny.

A special mention is due to the works of teams from France and Brazil, led by professors Bilal and Horn, which cover specific topics concerning the mineralogy and geochemistry of the environment (the phospho-gypsums from Morocco and the heavy metal contamination of Amazonian watersheds in the state of Minas Gerais)

The presence of authors from abroad – France, Brazil, Austria, Serbia, Iran, Morocco and the USA, is a good opportunity to discuss actual environmental problems related to the mining industry, not only from Romania, but also from countries with advanced expertise in this field.

In the end I wish to express my satisfaction and hope that the present SEGR symposium will be a good opportunity for discussion and know-how exchange among geologists, geochemists, miners and geophysicists, in the matter of environmental geology applied to mineral deposits.

Prof. dr. Gheorghe C. Popescu

President of the Society for Economic Geology of Romania



The idea of organizing a joint meeting of the Society of Economic Geology of Romania (SEGR) and Mineralogical Society of Romania (MSR) is a product of a good cooperation between the two societies having a common aim, i.e. the maintenance of the interest of colleagues in the fields of economic geology and of mineralogy. The added value is the constant attendance of colleagues from other countries at the previous symposia of the two societies.

The topics of the present joint meeting have changed now as a result of changing requirements of modern geology in general. The environmental aspects become more and more "pervasive" and the great number of papers dealing with such aspects is a good sign that the SGER (at least) is walking on the correct way.

The VIIth Symposium of the MSR is also an anniversary one, as the MSR is now 14 years old. Born in 1992 at the first meeting in Cluj-Napoca, the society meetings were further located in Timișoara (1993), Baia Mare (1995), Iași (1997), Bucharest (1999), again in Cluj-Napoca (2003), following a gap of four years. This gap is not very easy to be explained as a new gap of three years already occurred (2003-2006). Maybe the interest in mineralogy has decreased, maybe the attending possibilities were diminished, maybe the leader(s) of the society become tired. Nevertheless, this meeting can be seen as a revival of the MSR and will produce a new society council, after 14 years of only minor changes.

The papers to be presented at this symposium cover a large number of topics, i.e. different aspects of gold, gold ores and gold artifacts (Cojocaru et al., Damian & Damian, Udubasa et al.), diamonds (Iancu et al.), pegmatite minerals (Murariu & Raileanu, Mello & Bilal, Androne et al.), secondary minerals (Kristaly et al., Szakall et al.), as well as new data on a new fahlore occurrence (Neacsu et al.) and an extensive presentation of REE (and Y) minerals from the Ditrau massif (Hirtopanu & Udubasa). Results obtained from application of physical methods, Mössbauer, TEM/SAED, in the study of some minerals (S. Udubasa et al.) prompted a size-related classification of minerals to be developed (G. Udubasa et al.).

I'm happy that the descriptive mineralogy is still in use. Continuous investigations of the Ditrau massif (P. Hirtopanu) and in the last time of secondary minerals (Szakall, Kristaly) resulted in the increase of total number of valid mineral species in Romania to about 1200, i.e. more than one quarter of the minerals known. These last two topics produced "surprises" as concern some rare and expected or unexpected minerals and together with Bi-sulphosalts (Ilinca, Cook, Ciobanu, Damian) and cave minerals (Onac, Marincea, Dumitras) show that the

mineral occurrences in Romania are still far from being exhausted, even if some minerals are fine to very fine grained and enter the categories of infra- or nano-minerals. I would like to thank to the Hungarian colleagues for their interest in minerals from Romania.

Prof.dr. Gheorghe Udubasa
Member of the Romanian Academy
President of the Mineralogical Society of Romania

INVITED LECTURES



THE "IMPACT" OF ENVIRONMENT ON MINING

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INTRODUCTION

The mining industry is among the economic domains exerting a primary impact on the environment. Mining work sites are located in natural areas and landscapes which are directly affected by mining activities through: land occupation, concentration of soil, air and water pollution sources, depletion of non-regenerable resources, perturbation of wild life species and habitats, alteration of landform and landscapes, perturbation of communities by air pollution, noise and vibration, destruction of cultural heritage values, etc.

All these impacts have become reasons of concern for authorities in numerous countries, and legislative or procedural instruments have been established to reduce an often aggressive and non-sustainable character of the mining industry. This new attitude and vision has influenced even the financing institutions – which were the main sources for funding the mining projects, so that today, the capital credit granting has become subject to meeting social and environmental protection principles which are being strictly established through directives, policies, norms and guidelines issued by these institutions.

Even though for a given period in the past, the somewhat "spoliatory" character of mining seemed to be justified by an ever increasing demand of raw materials, the human kind has soon reached a stage of appropriate assessment for long-term environmental, social and economic costs of such an approach. Today, each mining project must observe to the highest detail, all potential impacts it might generate, and must ensure sound financial guarantees to mitigate such effects and to return occupied lands to a safe and stable after use. These liabilities have multiple derivations and complexities and have become one of the highly controversial points of the relationship between mining industry and the public or environmental authorities.

It is for this reason that the title chosen for this presentation might not be a just a mere quibble, but the expression of reality where mining industry has to confront sometimes – i.e. in cases of radical environmentalism – the very cancelling of its own initial objectives and

tasks. It becomes easy to argue that the need for economic development must go hand in hand with the social and environmental demands, and that every component within this triad can only exist by accepting the other two.

The present work summarizes several facets of the complex relationship and interdependency between mining and the environment.

1. The legislative and administrative framework

During the last decades, an ever greater attention has been paid worldwide to aspects concerning the impact of mining activities on the environment and the regulation of such activities with respect to environmental protection and rehabilitation.

Works and documents adopted by the UNEP (United Nations Environmental Programme) Conferences of Berlin on "Mining and the Environment" (1999) and "Mining and Sustainable Development" (2002), encompass exhaustive environmental issues related to worldwide mining.

The environmental legislation in some countries has a generic character and applies to all industrial branches. In other countries, i.e. of mining tradition, environmental regulations contain provisions that are specific to the mining industry.

In general, the administrative framework for environmental law application tends to be complex, with various ministry departments (e.g. ministry of the environment, ministry of waters, ministry of health etc.) having some attributions also in the field of environmental protection. Many countries have institutions (agencies) with specific attributions in a certain field of environmental protection (e.g. national parks, conservation and biodiversity, pollution, etc.). Moreover, in federal states such institutions exist both at national and regional (state) level.

In some countries, such institutional overlapping leads to conflicts between different ministries, departments and agencies with regard to law implementation.

The complexity of the administrative framework for environmental law implementation hardens the permitting process even in countries of wide institutional expertise and mining tradition. Many international companies consider that in some states of the USA and Canada, mining activities have become impossible to commission, not as much due to environmental restriction, but to a particularly cumbersome permitting process. The mining legislation in all states expressly mentions that the activity must comply with the

environmental legislation, and contains provisions related to the environmental protection, such as:

- Waste disposal;
- Water contamination;
- Soil erosion;
- Occupational safety;
- Chemicals and explosives handling;
- Environmental rehabilitation.

According to the mining laws/codes in most of the countries, a series of environmental studies are required in order to develop the activity, which, according to country and type of activity may contain one or more of the following:

- Environmental impact assessment or the report on environmental impact assessment;
- Environmental management plan;
- Environmental rehabilitation program;
- Mine closure and decommissioning plan and/or program.

In most countries, the general aspects concerning environmental protection, which are applicable to all industrial branches, are contained in an environmental law.

The individual instruments for environmental management are regulated by specific norms and usually include:

- Environmental impact assessment;
- Socio-economic impact assessment;
- Environmental management plan;
- Environmental monitoring program;
- Environmental audit;
- Environmental protection reporting;
- Environmental rehabilitation program;
- Mine closure and decommissioning;
- Compensation;
- Taxes and fees;
- Financial guarantees.

In many countries, the environmental law is added with a series of regulations relating to specific aspects of environmental protection, such as (Table 1):

- *Land law* – regulates the acquisition, use, management and protection of state owned land;
- *Soil law* – contains provisions related to soil contamination by chemical substances, residues, etc.
- *Forest law* – regulates the use of protection of forested areas, often with references to national parks and natural reserves;
- *Water law* – usually referring to both surface and underground water, it regulates the access to and the use of water resources, the discharge of wastewater into emissaries, as well as the water quality criteria and standards;
- *Air quality law* – regulates the atmospheric emissions and the air quality criteria and standards;
- *Biodiversity conservation law* – refers to the conservation of flora and fauna of scientific interest;
- *Parks and natural reserves law* – regulates the establishment and the management of parks and natural reserves;
- *Hazardous substances law* – regulates the transport, storage and disposal of toxic and dangerous chemical substances which sometimes, have specific provisions for cyanides;
- *Waste law* – regulates the disposal and elimination of various types of industrial wastes, sometimes with references to tailings generated by mining activities;
- *Construction safety law* – regulates various aspects concerning the safety of industrial constructions, with specific provisions, in some cases, to the stability of tailings ponds;
- *Occupational health and safety law* – refers to prevention of work accidents and occupational diseases;
- *Social protection law* – which, in countries of mining traditions, refers specifically to the loss of jobs following reduced activities or closure of mining operations;
- *Health law* – in some cases contains references to the quality of air and water, with view to the population health.

2. Instruments for implementing the environmental legislation

According to their political system, degree of institutional, economical and social development, cultural and mining tradition, different states may adopt instruments that are specific to one or more implementation policies of environmental legislation, such as:

- prescriptive policies (command-and-control);
- non-prescriptive policies (co-participative):
 - performance targets;
 - public consultation;
 - voluntary or negotiated agreements;
 - environmental management systems;
- economic instruments.

Prescriptive policies imply the enforcement and the strict observance of norms and standards concerning noxious emissions and the quality of water, air and soil.

Such norms and standards are usually established through regulatory acts and guidelines which add to the environmental law and which applies to all industrial branches, with no specific view to mining activities. They also do not take into account the local characteristics of the environmental factors or the seasonal variation of some of them. It is for this reason that experts consider such policies as leading away from optimal performance with respect to environmental protection and economic efficiency. Each mining operation has to be assessed and dealt with, according to the local conditions and to the specific aspects of the ongoing activities.

Non-prescriptive policies assume the implication of the operator in identifying the environmental problems related to the project, in finding the engineering solutions and in applying the most appropriate technologies for solving the environmental issues. Within such a system, the operator will establish and assume the performance objectives of the activities with regard to the environmental protection. It is self understood that such objectives will be reviewed and approved by the competent authority.

Table 1. Summary of Romanian environmental legislation

Environmental aspects	Main Authority	Relevant regulations
Air	MAPM	Environmental Protection Law No. 137/1995; Law No. 24/1994 (concerning the ratification of the Convention on Climatic Change); Law No. 8/1991 (concerning the ratification of the Convention concerning the transboundary and long distance atmospheric pollution); Law No. 354/1993 (to adhere to the Convention concerning the protection of the ozone layer); Law No. 111/1998 (adherence to the Convention concerning the fight against desertification); M.O. No. 462/1993 (air emissions); STAS No. 12574/1987 (environmental air quality).
Waste and wastewater	MAPM; The National Administration "Apelul Românesc"; local authorities	Environmental Protection Law No. 137/1995; Water law No. 107/1996; M.O. No. 396/1997; G.D. No. 1001/1990; G.D. No. 730/1997; NTPM 01/1997; NTPM 02/1997 (quality of wastewater effluents); M.O. No. 276, 277, 278, 279 and 280/1997.
Solid waste	MAPM; MIR Committee for Material Recycling; Inter-ministerial Committee	Environmental Protection Law No. 137/1995; Law No. 6/1991 (The Basel Convention); E.O. No. 33/1995 which has become Law No. 137/1996 (material recycling); G.D. No. 155/1999 (European Catalogue of Waste); E.O. No. 1621/1995 (waste recycling permitting); G.D. No. 340/1992; 437/1995 (the regime of waste import); Law No. 888/1992 (sanctions).
Mineral, oil and gas extraction	MIR; National Agency for Mineral Resources (NAMR); National Agency for Mining Areas Development and Reconstruction Programs	Mining Law No. 61/1998; G.D. No. 639/1998; E.O. No. 64/1998; G.D. 69/1998 (establishes the National Agency for the Reconstruction of Mining Areas); M.O. 72/1997, 90/1997, 101/1998, 103/1998, 130/1998, 96/1998, 96/1998, 6/1997 and 14/1997; G.D. 1043/1995; Law No. 70/1998; E.O. No. 49/1997 (oil extraction from the Black Sea); M.O. No. 48/1998 (sand exploitation).
Protected areas, parks and reserves	MAPM	Law No. 5/1991 (Deltas Convention); Law No. 13/1993 (Convention concerning wild life and habitat protection); Law No. 58/1994 (Rio Convention concerning biodiversity); Law No. 82/1993; G.D. No. 201/1994; G.D. No. 248/1994 (the Danube Delta); M.O. No. 7/1990 (national parks).
Forests	MAPM; National Administration of Forests	Law No. 26/1996; E.O. No. 96/1998 (The National Forestry Fund); Law No. 103/1996; Law No. 81/1993 and G.D. No. 82/1998 (Gaming and Fishing Fund); G.D. No. 350/1991 and 1044/1995; E.O. No. 27/1995; M.O. No. 171/1995
Land use	MAPM; National Administration of Forests	Law No. 18/1991, modified; Law No. 219/1996 (Concession Law); Law No. 151/1996 and G.D. No. 634/1998 (Regional Development of Romania); Law No. 33/1994 (Land expropriation for public utility); Law No. 69/1991, modified (local administration); G.D. No. 525/1996 (land use regulations); Law No. 27/1994 (taxes); G.D. No. 876/1994, 267/1995 and 786/1993 (land reclamation fund); Law No. 50/1991.
Public participation	Government authorities	Environmental Protection Law No. 137/1995; M.O. No. 125/1996 concerning the regulation of socio-economic activities with impact on the environment.
Free access to information and reporting requirements	Government authorities	Constitution of Romania; Environmental Protection Law No. 137/1995; M.O. No. 125/1996 concerning the regulation of socio-economic activities with impact on the environment.

In general, this system implies that the operator will draft and submit the following studies:

- the environmental impact assessment study;
- the socio-economic impact study;
- the environmental management plan;
- the environmental monitoring program;
- the environmental rehabilitation program;
- the mine decommissioning and closure plan.

The routine monitoring of the activity, with view to meeting the performance objectives is done by the operator or, in some countries, by independent institutions which are accepted by the government, operator and local community.

Experts agree that such a system has the advantage of taking into account the local environmental conditions (e.g. the assimilation capacity of the environment, background concentrations of contaminants, etc.) and the specificities of the activities being carried out by the operator.

Public consultation has been used lately in an increasing number of countries as a mechanism to identify project related environmental issues and to identify the technical solutions regarding the environmental management and activity monitoring.

The public consultation assumes the collective debate of the above mentioned studies and the amendment of these documents according to the results of the debate.

The implication of the local communities and of non-governmental organizations representing the interests of groups potentially affected by the mining operation, both in the permitting period and in the environmental management of the mining projects, represents a common practice in numerous countries.

Voluntary or negotiated agreements assume that the mining and exploration companies adopt codes referring to the environmental protection and rehabilitation as well as adherence to regional or international programs related to environmental protection

The environmental management system assumes the integration of environmental responsibilities into daily practices, through establishing organizational structures, responsibilities, procedures, processes and financial resources that would allow for a continuous improvement of the performances.

An environmental management system comprises several aspects:

- Assuming due obligations at all company levels, from the top management to the workers;
- Public assumption by the companies of the environmental policies which comprise aspects related both to the environment and to the social factors;
- Socio-economic impact assessment in relation to the company's activity.
- Environmental impact assessment related to the company's activity.
- Public consultation (local community, non-governmental associations, governmental authorities) during project design and operation.
- Establishing the objectives and targets regarding, for instance:
 - Performance levels;
 - Mitigation of environmental impact
 - Non-mining waste recycling;
 - Abatement of water volumes used in mining activities;
 - Public access to information, etc.
- Drafting of a management plan to encompass the procedures and methods by which the company will attain the environmental protection objectives;
- Drafting of documentations and manuals that would contain the clear, explicit and detailed strategies, policies, procedures and responsibilities concerning the environmental protection;
- Establishing the concrete procedures regarding the operational control in emergency situations, for each activity and working site;
- Drafting and implementation of a periodical staff training program;
- Performance monitoring concerning noxious emissions;
- Environmental performance and compliance audit;
- Review and continuous improvement of the environmental management system.

Companies may establish their own environmental management system or they may adopt a standard system which will require specific certification (e.g. ISO 1401, EMAS). IN some countries, the application for and the issuing of such a certificate by a company ensures that the activity of a certain company develops in a first stage, according to a minimal standard and follows a path of continuous improvement of environmental performance.

In any country, the environmental legislation contains a series of **economic instruments** which allow the authorities to intervene in cases when the operator does not carry out appropriately its activities and does not fulfil the imposed or assumed environmental obligations during the operational cycle or in case of environmental accidents.

Some countries resort to economic instruments which encourage the operators to improve their environmental protection performances (e.g. pollution abatement, use of modern technology, etc.)

Last but not least, the economic instruments are used by the state to ensure that the operator fulfils all its due obligations regarding the rehabilitation of the environment at the cessation of activity, or, in case of non-compliance, the operator will pay practically all the costs incurred by environmental rehabilitation.

The economic instruments differ from one country to another and depend on the regulation policy – prescriptive or non-prescriptive, adopted by that country.

Such instruments include:

- Taxes and fees;
 - Financial instruments derived from the operator's legal liabilities;
 - Guarantee financial instruments;
 - Incentive financial measures.

Environmental rehabilitation costs incurred at the closure of a mine are, as a rule, high and trigger high financial guarantees. The amount of such guarantees depends on the conditions imposed for environmental rehabilitation. There are several approaches in this respect:

- In some countries, the financial guarantees are established based on the estimated costs for rehabilitation of environmental factors, in accordance with several quality standards. In some cases it is considered that the land must be brought to its pre-operation status.
- Due to the fact that the estimation of environmental rehabilitation costs cannot be totally accurate, some countries take into account the related risk factors.
- Given that, at least in some cases, the environmental rehabilitation requires also other activities such as long term monitoring (e.g. the quality of waters affected by ARD runoffs from waste heaps), some states take into account also the costs of such operations. As the final costs in the case of long term monitoring may be significant, some countries apply a gradual or incremental system of financial guarantees that will not affect the economic viability of the project.
- Some land affected by the mining activity, may be rehabilitated before the final mine closure. The rehabilitation of such areas during the mine life cycle has

become a common requirement from the environmental authorities in many countries and a routine practice of mining companies.

The financial guarantees for environmental rehabilitation are usually established at the beginning of the project, based on the information contained in the environmental documentation required for environmental permitting (e.g. the report for the environmental impact study and the mine closure and rehabilitation plan) and they are subjected to reviewing during the operation.

The amount of financial guarantees is established by two main methods:

- affected surface – the financial provision (the guarantee) is calculated by multiplying the surface with the unitary (standard) rehabilitation costs;
- project data - the financial provision (the guarantee) is calculated based on all aspects related to the rehabilitation of the area, and which are reviewed independently, on the basis of project duration.

Table 2 summarizes the calculation methods used for the financial provisions (guarantees) in several countries.

The financial guarantee instruments (Figure 1) are different from one country to another and may include:

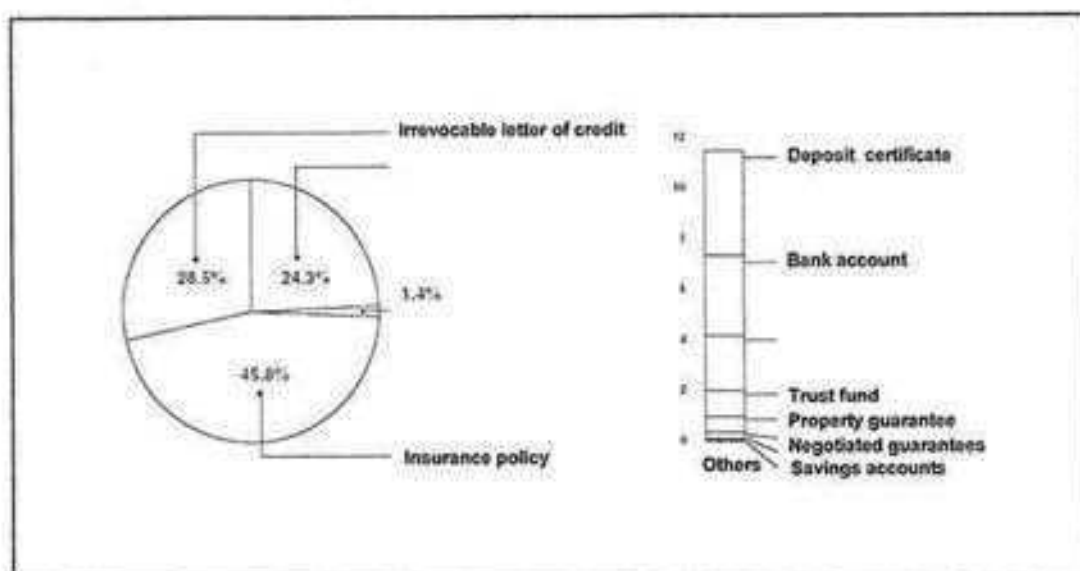
Table 2. Methodologies used for calculating the amount of financial provisions for environmental provisions in several countries.

Country	State	Methodologies used for calculating the amount of financial provisions
USA	Federal level / Colorado	Direct remediation costs (e.g. profiling, revegetation, demolition and removal of unusable structures, etc.) and indirect costs (e.g. mobilization/demobilization, contingency costs, replanning of expenses and fees provisioned by the contract) stated in the protection and rehabilitation plans. For the calculation of guarantee, specialised software provided by the competent authority is used.

Canada	British Columbia	The following facts are taken into account: disturbed surface (ha), rehabilitation costs (USD/ha), investment and operational costs related to the post-closure stage, included in the permitting documentation, including a plan of all proposed works and a protection and rehabilitation program for the land and water streams affected by the mining project. For the calculation of the financial guarantee, special software delivered by the competent authority is used.
	Northern Territories	The guarantee is established taking into account the type of operation, types of waste, buildings and equipment used, chemical substances and soil management, mobilization/demobilization costs, post-closure costs, project management, water treatment during post-closure stages, total annual costs. Costs are calculated by means of special software named RECLAIM.
Australia	Queensland	For exploration activities, the guarantee is established on the basis of the surface to be affected and of the risk degree related to the scheduled activities. For mining activities, the guarantee is established based on the affected surface and on the fees per surface unit, established for each separate activity, by multiplying the unitary cost with the total affected surface. Incentives are granted with view to environmental compliance (up to 75% discount of the calculated values of the guarantee, depending on the type of activity).
	West Australia	Fees are different and range between 5,000 \$/ha for areas with low mobilization costs, and 15,000 \$/ha for very isolated areas.

- **A money deposit in a special account** - In some countries, both the competent authority and the company have access to this account, the later however, only for using the funds for environmental rehabilitation purposes.

- **Irrevocable letter of credit** – involves the signing of an agreement between the company and the bank based on which it assumes the financial responsibility, within the terms stated in the letter of credit, in the case the company does not fulfil its environmental obligations.
- **Performance guarantee** – involves an insurance policy issued by an insurance company through which it assumes financial responsibility up to an amount to be established through the insurance contract, for all the environmental issues stated in the rehabilitation plan.
- **Insurance policy** – involves assuming financial responsibilities by the long-term (several years) issuing financial institution, within a total amount provisioned in the insurance contract.
- **Trust funds** – assumes the company's contribution with certain amounts to an investment fund (similar to a private pension fund) which is managed by a third-party.
- **Guaranteeing by the mother company** – in the case of international mining corporations, the mother company may assume responsibility to fulfil the contract obligations concerning environmental rehabilitation to which the operator in a certain country has committed to.
- **Mortgaging of assets** – involves mortgaging the equipment in the favour of the state, which has the right to sell the assets in case of non-conformance, to cover the



rehabilitation costs.

Figure 1. Ratios of various guaranteeing financial instruments used in the USA for the environmental protection and rehabilitation (US Government Accountability Office, 2005).

3. International initiatives and principles

During the last decades, environmental protection and rehabilitation issues have crossed the borders between countries. Treaties and conventions impose signer countries with a series of norms and restrictions concerning the development of mining activities with regard to environmental protection and rehabilitation.

Several codes and guidelines concerning the protection and rehabilitation of the environment have been drafted by international institutions (e.g., the United Nations, World Bank), and adopted already by some mining companies.

Such codes and guidelines refer to:

- The principles which have to govern the activity (e.g. the principles of sustainable development);
- The environmental management (e.g. risk assessment and management);
- Performance criteria (e.g. technical criteria, ethic codes, best practice guidelines, etc.);
- Particular aspects of mining activity (e.g. environmental protection during exploration activity, design and management of tailings ponds, cyanide management, etc.);

The principle of sustainable development has lately become the core element of the environmental legislation in many countries, of the environmental policies of mining companies, of the investment policies and of monitoring activities carried out by numerous non-governmental organizations involved in the protection of the environment.

The principle of sustainable development, was firstly defined in 1992, at the meeting in Rio de Janeiro. It stipulates that the "present generation must fulfil its needs without compromising the possibility of future generations to fulfil their own needs".

Recently, the principle has acquired new facets. Besides the basic concept of intra-generation, the sustainable development principle includes now a series of new concepts.

The **intra-generation principle** involves the equitable distribution of costs and benefits within a generation. In other words, the sustainable development assumes the integration of economic, social and environmental costs and benefits generated by a project, in a manner which is equitable both to the mining company and its shareholders, on the one hand, and for the local community and the society, on the other hand.

Any mining project has the purpose to bring financial benefits to the company and to its shareholders. On the other hand, the development of a mining project, involves the creation

of new jobs, both in the ore mining and milling part and in the ancillary technical field (e.g. manufacturing of equipment, maintenance of equipment, etc.), as well as in the commercial (e.g. shops) and social (e.g. schools, hospitals, libraries) domains, etc.

As per the observations above, few new principles represent the today's ground of sustainable development.

The implication of the community in the mine design and permitting activities, by means of public meetings around the project, allows the identification of:

- Community position with regard to the project development;
- Sensitive project aspects require special attention;
- Technical solutions.

The participation and partnership among the community members with respect to the environmental management of a mining project, guarantees:

- the taking into account of interests of all parties;
- the full understanding of the risks, implications and consequences incurred by certain decisions;
- the accountability of all parties, with regard to the implementation of adopted decisions.

The accountability of all parties, including the company, the local communities, non-governmental organizations and the authorities, with regard to the decision and actions taken, represent the key to sustainable development of a mining region, and implies:

- obtaining benefits for all stakeholders (profits for the company and shareholders, jobs for the local communities, taxes and fees for the local and central authorities, benefits for the society);
- achieving the equilibrium between the benefits generated by exploiting the mineral resource and the potential impact of the activity on the environment;
- creating an infrastructure which, following the cessation of the mining activity, would allow its long term use in the development of other industrial activities;
- ensuring the transparency of the management and decision making process in order to reduce the concern of the local community with regard to the social and environmental impact of the project and to avoid mining activities being seen by the society as undesirable;
- efficient use of energy, water, land and mineral resources;

- application of modern technology able to ensure economic efficiency, high environmental protection standards and rational exploitation of mineral resources.

The application of sustainable development principle implies transparency, dialog and openness from all stake holders, with its success depending on their cooperation.

Finally we would like to underline that blocking a mining project does not necessarily mean a socially and environmentally responsible attitude and does not guarantee the sustainable development of a certain area.

TARA MOTILOR (MOTZILOR COUNTY): GEOLOGIC AND METALLOGENETIC FEATURES TOGETHER WITH SOME ETHNOLOGIC ASPECTS

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Albac, a historical locality from Apuseni Mts becomes the host-plan of the 5th National Symposium of Economic Geology. This is a rare opportunity for us to present some features characteristic to Motzilor County (MC). These features include an overview on the geology and on the principal mineral deposits within this territory that allow, afterward, some digressions to ethnologic aspects. These aspects are in agreement with the topic of the mentioned symposium. The notion of "Tara" derived probable from "Terra" – and signifies a territory well marked geographically or geomorphologically having proper ethnologic and cultural characteristics. Similar to other Romanian ethnologic entities such as Bucovina, Maramures, Tara Barsei a.s.o., "Tara Motzilor" (MC) has its specific cultural landscapes.

Geographycal M.C. s.s. occupies a territory from the upper basin of the Aries River, upstream of Bistra locality, with their tributary effluents; in a broad sense (s.l.) it may extend up to Lupsa and Baia de Aries localities (Abrudeanu, 1928). According to Mihailescu (1963) as a geographical division of the Apuseni Mts., the Motzilor County occupies the south eastern part of the Biharia Mts., with Curcubata and Gaina Massifs, as well as the "Golden Mountains " (Munczii Auriferi ac. to Mihailescu) or Abrudului Mts. (after Abrudeanu) as part of the Metaliferi Mts. (fig 1).

1. Geologic setting

So defined, MC covers a territory belonging to the North Apuseni Mts, as well as to the South Apuseni (Metaliferi Mts.) and therefore this is characterized by a very complex geologic and tectonic constitution. For the most part, the North Apuseni Mts. are built up of Precambrian and Paleozoic metamorphic and sedimentary formations, as well as Mesozoic magmatic Formation, integrated in the Bihor Autochthonous Unit, the Codru Nappe System and in the Bihor Nappe System; whereas the South Apusenides (Metaliferi) are formed mainly of Mesozoic and Tertiary sedimentary formations and Neogene volcanic products. All of them belong to the Transylvanides geotectonic unity (Sandulescu, 1984, Balintoni, 1998).

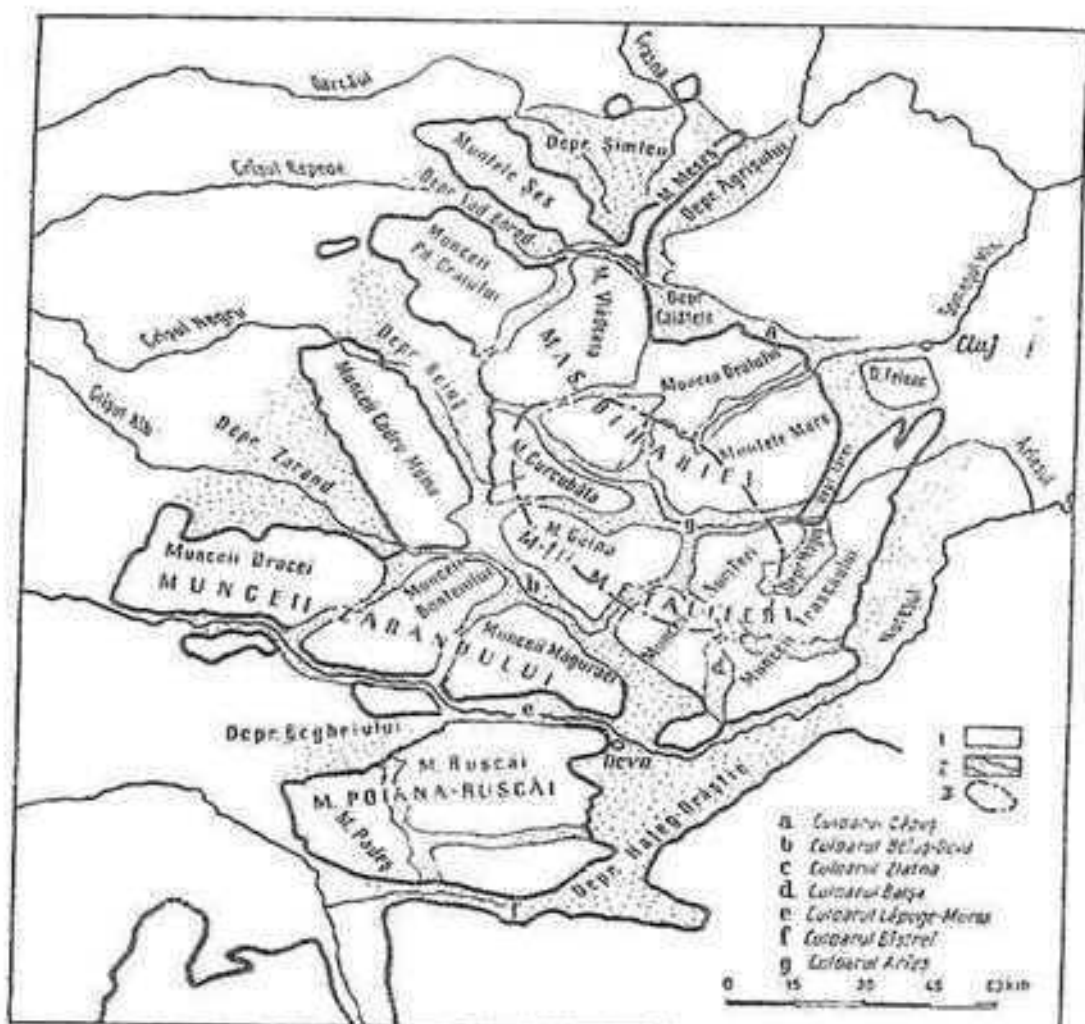


Fig. 1 The position of the Motzilor County in the geographical units of the Apuseni Mts., (according to Mihailescu, 1968) 1. Massive, 2. Depression and high plateaus, 3. Motzilor County, approximate limit.

The Upper Cretaceous-Eocene magmatic intrusions, well developed in the Bihor Mts. represent the northern part of the Laramic-Banatitic Province (Giusca, Cioflica, Savu, 1966). This magmatic belt, with a NE regionally trend cuts the Alpine structures of the Transylvanides as well as the Biharia and Codru Nappe Systems together with the formations of the Bihor Autochthonous Unit (fig. 2).

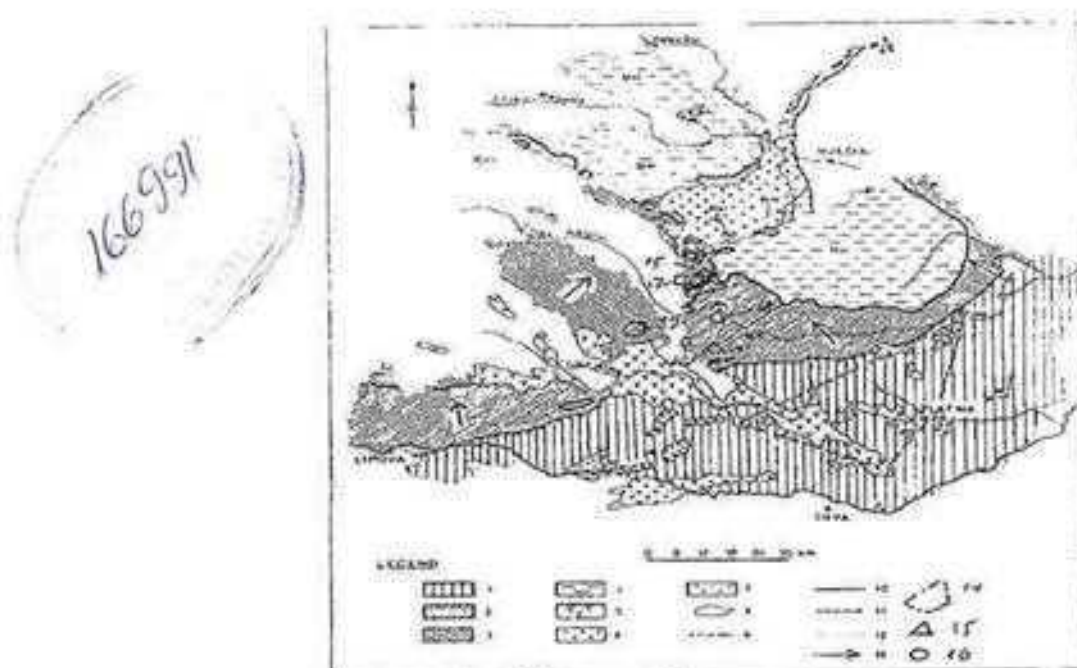


Fig.2 General tectonic sketch of the Apuseni Mts. (acc. to Balintoni, 1998)

1, Transylvanides; 2, Biharia Nappe System; 3, Codru Nappe System; 4, Bihor Autochthonous Unit; 5, Neogene volcanics; 6, Upper Cretaceous banatites; 7, Eocretaceous arc granitoides; 8, Magmatite boundary; 9, Transylvanides front; 10, Pre-Gossau overthrust; 11 Tertiary Mezes thrust; 12, transgression; 13, sense of tectonic transport. 14. Gold Quadrangle; 15-16 Laramian mineralisations: 15- Baita Bihor, 16- Brusturi; 17-19 Variscan mineralisations: 17 - Bihor U-mineralization, 18 - Avram Iancu Co-Ni-U mineralization; 19 - Rarusu U-Mo mineralizations.

2. Mineral deposits and occurrences

In the MC and neighborhood areas there are known a variety of occurrences and mineral deposits, related to different host rocks, from Precambrian to Tertiary or more recently.

2.1. Products of the Variscan metallogenesis are represented by the modest magmatic concentrations of magnetite bodies, the chlorite-albitic schists from Biharia Series. Such occurrences were described by Giusca (1960) upstream of the Ariesul Mic and by C. Ionescu (1971) in Leucii Valley, in the same Biharia Series (Ivanovici et al., 1976). To be mentioned, are also, some volcano-sedimentary concentrations of Mn minerals in the Paleozoic metamorphites of the Baia de Aries Series and in the Muncel Series (Bihor Mts.); as well as some Cu-pyrite mineralisations, as those of Cioara Valey (effluent of Aries River in the same Baia de Aries Series).

2.2. For the Variscan metallogenesis from Bihor and Codru geotectonic units significant are the occurrences of the U-mineralisations. Mentioned by Klockmann in 1924 (in Ivanovici et al., 1976) such occurrences were investigated during the 5th decade of the last

century by Russian geologic expedition and, later, by Romanian explorer. Only some recent published data may be used to outline some interesting features of such mineralisations.

a) in the Bihor Mts. such mineralisations are hosted by a complex of metapsamitic rocks consisting of quartzites and metagraywakes with intercalations of phyllites of Carboniferous age. At Budureasa and Ferice the occurrences of U-minerals were identified in a sequence of Permian sandstones and tuffites, whereas at Pietroasa (Bulz and Valea Rea prospects) the U- mineralisations are hosted by the Triassic (Scythian) gray-green sandstones containing incarbonised vegetal substances. All these formations belong to the Arieseni series (nappes); there are some evidences of presence of the "red bed" facies of mineralisations, as in the Padis area.

The uranium mineralisations consist of pechblende and "uranium black" associated with supergene products of alteration, i.e. "uraniferous micas": becquerelite, uranophane, autunite, torbernite, cuprosklodowskite (Hagea and Hagea, 1994), kasolite – $Pb_2(UO_2/SiO_4)2H_2O$ and zeunerite $Cu(UO_2/AsO_4)_2 \cdot 10H_2O$. To these minerals some Co-Ni minerals may be added: linneite, polydymite (Ni_3S_2), safflorite-rammelsbergite and sulfides (B.G.P.C.), arsenopirite, tetrahedrite-tennantite, bourmonite; occasionally aikinite and, in some specimens, magnetite, hematite and as a rarity, Be-silicates (Matyasi, 1999). These mineral associations constitute thin bands, lamines, nests, impregnations and veinlets in the sedimentary host rocks, mainly in a gray-green sandstone containing incarbonised vegetal substances.

The morphology, mineral paragenesis as well as the geologic boundaries support the idea that U-mineralisations from the Bihor massif have a sedimentary-syngenetic genesis, with some epigenetic remobilizations (Matyasi, 1999). These epigenetic remobilizations may be due to the fluide emissions from the laramic-banatic magmatites.

The "Avram Iancu" Co-Ni-U mineralization situated on the southern slope of the Biharia (Curcubata, 1851 m) Peak, on the uppermost stream of the Ariesul Mic river. It differs to some extent from the above mentioned mineralisations. This is located in a petrographic sequence of the Biharia Nappe that consists of porphyroblastic-albitite-chlorite shists, amphibolites and crystalline limestones and dolostones. The rocks exhibit hydrothermal alteration due to the proximity of the laramic intrusions.

Three types of mineralisations were distinguished: (a) Co-Ni-U; (b) chalcopryrite-pyrite; (c) Pb-Zn-Cu (Zajzon et al, 2006). The following mineral associations were identified: nickeline, skutterudite, cobaltite, gersdorffite, sulfides (Py-Cp-B-G), brannerite (UTi_2O_6), uraninite and zircon as accessory mineral; annabergite and erythrite are the main alteration minerals, identified by XRD (Zajzon et al, 2006).

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According to some opinions, this mineralization resembles the classical pentametallic formation from the Erzgebirge deposits, in Germany. This is however an incomplete paragenesis. Its genesis may be due to the mobilization of the ore component by hydrothermal fluids derived from deeper laramic intrusions. The Fe-Mg silicates of the host rocks favoured the crystallisation of the mineral phases.

As an additional case to the above mentioned U-mineralisations from North Apuseni Mts., some aspects of the Ranusa mineral deposit should be mentioned. This is an U-Mo type of mineralisation. Together with the Zimbru Cu-Mo-U mineralization (Salajan, 1970) these deposits belong to the Moma tectonic unit, as part of the Codru Nappe System, situated at 9 Km of Moneasa Spa; the Ranusa mineralization is hosted by the Permian Lower Rhyolite Formation of ignimbrites. The mineral paragenesis consists of pitchblende, molybdenite $\pm$ joseite, ilsemanite; and by urano-molybdate (umohoite, iriginite, moluranite), uranium black, torbernite, autunite, uranophane, wulfenite associated with some skutterudite, nickel-skutterudite and chalcopyrite, pyrite, galena, tetrahedrite, hematite and barite (Matyasi et al, 2000). The analytical data point out to some positive geochemical correlations ($r = 0,8-0,9$) as: U-Cu, U-Mo, Mo-Bi, Bi-Co. The presence of Li completes the geochemical paragenesis of the U-Mo mineralization (Matyasi et al, 2000).

The U-deposits and occurrences from the North Apuseni metallogenetic district emphasize interesting similitudes to some European ones. In Europe, many U-deposits are either of Permian age, or are located in, or close to Permian sedimentary rocks. From the point of view of U-metallogeny, the Permian period was important because (1) the sediments were deposited under contrasting redox conditions, (2) the intense surface weathering was favorable to U-leaching, (3) volcanic emission were significant and (4) the intense tectonic movement facilitated fluid circulation in the sedimentary basins and in the basement (Pagel, 1990). The analytical data mentioned by Matyasi (1999) reveal a relative high geochemical background of U in the samples of crystalline rocks (4,048 ppm U) and for the samples of Permian ignimbritic rhyolites (2,471), more than double higher than to the granodiorite-banatic samples. So, the source of U (as protore) may be found in the basement crystalline rocks – especially in the high feldspathic varieties and /or in the Permian felsic – ignimbritic rocks. Significant is also the presence of topaz, near zircon, as accessory minerals in some samples of Permian rhyolite from Bihor Mts. (Lidia Jude, 1971).

2.3.1 Alpine Laramic minerals deposits

The products of the metallogenesis from Bihor massif reveal interesting relationships with the Laramic-banatic magmatites from Budureasa and Pietroasa, on SE border of the Vladeasa volcano-plutonic complex; a series of magmatic intrusions occur in Biharia and

Gaina massifs and further away to Halmagiu nearby Crisul Alb river. The petrographic terms follow a succession from diorites-microdiorites, or monzodiorites to granodiorites and granites, even monzogranites ones. Smaller intrusions of felsic-rhyolitic rocks and system of dykes of basaltic andesites, basalts and lamprophires, of NW-SE trend, close the succession of the laramic magmatites (Jude, Stefan, 1967, Istrate, 1978, Stefan et al. 1992) Only in a favorable geologic context (structure) such magmatic intrusions may be mineralized. The most important mineral deposit, Baita Bihor is formed in the cupola of a granodiorite-granit pluton, installed in a tectonised, dominantly carbonatic, Mesozoic rocks, partially covered by the Arieseni Nappe with Permian detritic rocks. Large halos of thermic and metasomatic products accompany the plutonic intrusion: calcic skarns with grossular, andradite, vezuvian, wollastonite and diopside in Mesozoic limestone; magnesium skarns with diopside $\pm$ forsterite and phlogopite, humite-clinohumite-chodrodite in Carnian dolomite.

It was supposed that the mineralization is differentiated according to the host rocks: (a) Mo-Bi and Cu-W in Ca-skarn; (b) Cu-W-Bi in Mg-skarn, replacing Carnian dolomite; (c) Boron mineral type in magnesian hornfels (Cioflica et al., 1977, Marincea, 1993). In the category of nonmetallic concentrations need to be mentioned: (a) wollastonite concentrations in Ca-skarn with Mo-Bi mineralisation, as those along the Blidar tectonic line; (b) brucite concentrations "predazzite" – in the hornfelses within dedolomitized marbre at Baita Bihorului, Pietroasa and Budureasa deposits; (c) concentrations of garnet minerals in the Cu-skarns and Mg-skarns. To be mentioned are also the polymetallic mineralisations from the southern side of Bihor Mts. as hydrothermal periplutonic ore deposits: Brusturi Cu-Py($\pm$ Pb-Zn) and Luncoara Pb-Zn (Au) mineralizations. There is uncertain whether the outcrops of baritic veins in the crystalline shists of Biharia and Muncel series (Scarisoara-Ariesul Mare; Sturu peak-Biharia) and Permian formations (Biharia and Ranusa) belong to Laramian or to the Variscan metallogenesis.

2.3.2. Neogene ore deposits

Four important ore deposits from the South Apuseni Mts. belong to the MC (Tara Motilor): Baia de Aries, Rosia Montana, Rosia Poieni and Bucium. They mark the NE corner of the Golden Quadrangle within Metaliferi Mts., each with his characteristics. The Baia de Aries is an Au and Au-Ag deposit with tellurides in upper Miocene andesitic rock and a hydrothermal-metasomatic base metal deposit in the Paleozoic crystalline limestone and in Neogene eruptive breccias; Rosia Montana, an authentic golden deposit, with Au-Ag and small occurrences of tellurides; Rosia Poieni, a porphyry Cu-Au type of mineralization; whereas Bucium include either epithermal Au-Ag, Cu-Py $\pm$ As and polymetallic veins as well as a porphyry style in the Tarnita subvolcanic intrusion.

The Baia de Aries Au and Au-Ag mineralisation occurs as thin veins, mineralized eruptive breccias and as stockworks adjacent to the breccia pipes related to extrusive cupolas and to subvolcanic bodies of Sarmatian Qz-andesite. Five mineralized breccia pipes, were exploited in the last century.

The gold occurs as microscopic grains associated with quartz, sulfides and sulfosalts, in veins and in eruptive breccias, as free gold; as tellurides ("Sylvanite Vein") and as "invisible gold" in arsenian pyrite, the so named "Golden pyrite" and in arsenopyrite, e.g. in the collapse breccia within 'Concordia' (no.1) breccia pipe (Cochet, 1958, Ghitulescu, Socolescu, 1941). In this case, the gold was recovered by modern cyanuration processing. (fig.3)

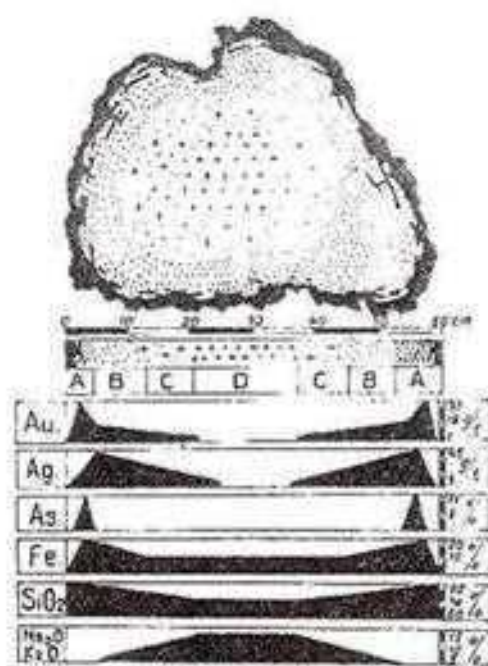


Fig. 3 A clast of andesite within Collapse breccia. " Concordia breccia pipe" covered by a cruste of "golden quartz" invisible gold in arsenopyrite. (In Cochet R., 1957)

The native gold is a variety of "cuprian gold" with a composition of 13% Ag and 23% Cu (Radut, Constantiniuc et al., 1985, in Cioflica et al, 1999). The samples of gold have a yellow colour with reddish tint.

Rosia Montana

The famous gold deposit Rosia Montana is known and mined before the Roman colonisation of Dacia.

It is located in a small basin of volcano-tectonic collapse in which the crystalline basement and Cretaceous formations are covered by Miocene volcano-sedimentary deposits, the so called "Local Sediment" by Posepny, with clasts of rhyolite in the tuffitic sequences

(Cioflica et al., 1973). This volcano-sedimentary deposit was pierced by some extrusive domes of Badenian dacites (13.5 Ma) and by Sarmatian andesites (9.3Ma) (Rosu et al., 2000).

The gold mineralisations are distributed on the whole Miocene basin, but the maximum concentration is related to the Cetate and Carnic extrusive domes and to some subvolcanic bodies. It constitutes veins, sets of veins and a lot of mineralized breccia pipes bordered by golden stockworks ("volburi"). In the adjacent areas there are the Tarina – Orlea, Igre, Vaidoia groups of veins within Miocene sedimentary deposits (Ghitulescu, Socolescu, 1941). The so named "Glamm breccia" (glauch) that partially border the Cetate hill (Palfy, 1915) is a polymictic breccia with class of crystalline schists Cretacic sedimentary rocks and dacite fragments in a matrix of fluidised argillitic and psamitic material. A pervasive hydrothermal alteration with quartz and adularia, affect a great part of the Cetate and Carnic dacitic hills. The Roman old galleries in the Cetate hill prior the quarry-mining had an aspect of "Middle ages fortress" (fig 4).



Fig. 4 Cetate Hill from Rosia Montana in 1957. The traces of ancient mining works

The mineralisation is dominant auriferous with free gold and microscopic native gold associated with some sulfides (B, G, Cp, Py) and sulfosalts (tetrahedrite, bourmonite etc.) in a gangue of quartz, carbonates and rocky material; some veins of Carnic massif were the richest in sylver minerals: argentite, proustite, pyrargirite, polybasite-pearcerite, stephanite (Petrulian, 1934). New data point out to the presence of the tellurides. The fineness of native gold cover an interval of 500‰ to 700‰ (Petrulian, 1934) characteristic to the epithermal gold deposits. $^{40}\text{Ar}/^{39}\text{Ar}$ radiometric data on hydrothermal quartz from a quartz-adularia –pyrite vein from Cetate pit, yield ages of 12.78 ± 13 Ma (Manske, 2004). This denotes that the gold mineralisation is 1Ma younger than the host dacitic rock.

3. Some ethnologic and environmental aspects.

Who are "moții" (Motzii)?

The simplest answer is that they are an old Dacians population with some supplement (addition) of Roman colonists and influences from other peoples. As one evidence is the great diversity of the names. A population of shepherds and temporary miners in the neighborhood mines. The mountain landscape and the nature of soils make the agricultural occupation practically improper. The writer Geo Bogza qualifies this territory as "Tara de Piatra" (the Stone County). So, the principal constrain was in the past to earn daily bread; with other word, to gain the cereals for food. To solve this problems the men migrated episodical by to plains, to Banat and Crisana counties and, after 1918, in the "Old Kingdom" (Muntenia and Oltenia provinces) and carried in the cartfuls their woody products: casks, tubs, kegs, wooden pails a.s.o. Thus, they obtain by exchange the necessary cereals and other commodities for family. The gain the cereals had as effect the proliferation of the hydraulic mills, along the principal rivers; until the middle of last century.

The wood bugle (buciumul) and the "Targul de fete" (The girls market) on the Gaina Mountain are between the most characteristic ethnologic features of this population, as well as the woody pan (saitrocul) in the mining areas. The "Targul de fete" on the Gaina Mountain was and is the most important event in a year. In the spring the shepherd climbed up with their animals on mountain and in summer, they climbed down for moving the herbs, necessary as animals' foods in the winter season. This "market" takes place in a Sunday, near 20 July and is celebrated with the participation of the neighborhood population and during the time by many tourists. At this mountain market one may find agricultural tools, handicraft wares etc.



Fig. 5. Bedeleu (Trascau) ridge of Portlandian limestone, allong of the Arias River. Foto Puscariu V. in Ilie M., 1957. In landscape, a caravane of cartfuls: motzi that descend to the plain.

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SOME GEOLOGICAL AND ECONOMICAL ASPECTS IN USE OF GEOTHERMAL ENERGY IN ROMANIA

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Key words: Geothermal Energy, Romania, direct use

Romania's geographic location, overlapping the Carpathians (the most north-eastern branch of the peri-Mediterranean Alpine folded belts) and their foreland, accounts for numerous occurrences of geothermal resources of moderate enthalpy. Almost within each major tectonic unit of these areas the concentration of geothermal resources was inferred either from surface manifestations as thermal springs or from deep boreholes exhibiting temperatures higher than "normal".

Exploration for geothermal resources began in Romania in the early 1960's, arising from a hydrocarbon search program, which as an unexpected benefit also identified eight promising geothermal areas. Within these areas, over 200 wells, drilled to depths between 800-3500 m, show the presence of low- enthalpy geothermal resources (40-120°C). Completion and experimental exploitation of over 100 wells during the past 40 years has enabled evaluation of the exploitable heat available from these geothermal resources. Proven geothermal reserves in



Figure 1: Location of the Romanian geothermal reservoirs

Romania are currently about 200,000 TJ for 20 years.

The principal Romanian geothermal resources are found in porous and permeable sandstones and siltstones (for example, in the Western Plain and the Olt Valley), or in fractured carbonate formations (Oradea, Bors, North Bucharest). The total thermal capacity of the existing wells is about 480 MWt (for a reference temperature of 25°C). Of this total, only 152 MWt are currently used, from 96 wells (of which 35 wells are used for balneology and bathing) that are producing hot water in the temperature range of 45-115°C. For year 2000, the annual energy utilization from these wells was about 2,900 TJ, with a capacity factor of 0.6. More than 80% of the wells are artesian producers, 18 wells require anti-scaling chemical treatment, and six are re-injection wells. The main direct uses of the geothermal energy are: space and district heating 37%; bathing 30%; greenhouse heating 23%; industrial process heat 7%; fish farming and animal husbandry 2%.

Fourteen new geothermal wells were drilled in Romania with National financing (National Geological Program). Three additional wells are in progress at this writing. Of the first fourteen, drilled to depths ranging from 1500 m to 3500 m, only two were non-producers, for a success rate of 86%.

Tabel 1. Main Parameters of the Romanian Geothermal Systems

PARAMETER	U/M	Oradea	Bors	Western Plain	Olt Valley	North Bucharest
Type of Reservoir		Fissured Carbonate	Fissured Carbonate	Sandstone	Gritstone	Carbonate
Surface	Km ²	75	12	2500	18	300
Depth	Km	2.2-3.2	2.4-2.8	0.8-2.1	2.1-2.4	1.9-2.6
Drilled Wells	(total)	14	6	88	3	11
Active Wells		12	5	37	2	5
Well Head Temperature	°C	80-110	120	60-90	90-95	60-80
Temperature Gradient	°C/km	35-43	45-50	38-50	45-48	28-34
Total Dissolved Salts	g/l	0.8-1.4	12.0-14.0	2.0-7.0	13.0	2.2
Annual Savings	toe	9700	3200	18500	2600	1900
Total installed power (with existing wells)	MWt	58	25	210	18	32
Exploitable Reserves (for 20 years)	MW/yr	570	110	4700	190	310

The development of direct utilization of Romanian geothermal resources (Table 2) has been hindered considerably by the inevitable difficulties attending transition from a centrally planned to a free market economy, as well as by operational capabilities which in some cases

have not kept pace with recent technological advances. As a result, current geothermal production falls far short of the country's remarkable demonstrated potential.

Referring to the personnel allocated to geothermal activities it is observed that there has been a decrease of about 20% in personnel with university degrees, especially in industry (represented by Foradex and Transgex, both in the process of privatization) where during the last five years the decrease has been 25%. During 1995-1999 the total investments in geothermal projects (Table 3) were 24 million \$US, 12% less than during 1990-1994 and 28% less than during 1985-1989 respectively, all projects being funded from the State Budget. Out of the total investments in geothermal projects the cost of drilling the 14 wells represents 70%, the rest (30%) being invested in direct use.

Table 2. Summary of geothermal direct heat uses in Romania

Use	Installed Capacity (MWt)	Annual Energy Use (TJ/yr)	Capacity Factor
Space Heating	53	1073	0.64
Greenhouse Heating	40	665	0.52
Fish and Animal Farming	3	60	0.63
Industrial Process Heat	14	201	0.45
Bathing	42	871	0.65
TOTAL	152	2870	

Table 3. Total investments in geothermal (in million USD)

Period	Research&Development (incl. surface exploration&exploration drilling)	Field Development (incl. production drilling&surface equipment)	Utilisation		Funding type	
			Direct Heat	Electrical	Private (%)	Public (%)
1990-1994	21	7	5	0		100
1995-2000	15	5	7	0		100
2000-2005	8	10	6	0		100

The main obstacle to geothermal development in Romania is the scarcity of domestic investment capital. In order to stimulate the interest of potential investors from developed countries, and to comply with the requirements of large international banks, an adequate legal and institutional framework has been created, adapted to a market-oriented economy. However, legislative documents of interest for geothermal energy use have been issued in the last ten years: Mining Law (No. 85/2003, replacing the Law 61/1998); Government Decision No. 1208/2003, Water Law (No. 107/1996), Environmental Protection Law (No. 137/1995 modified by Law 159/1999).

MICRO-, INFRA- AND NANOMINERALS AND THEIR BEARING ON MINERAL SYSTEMATIZATION AND ORE CHARACTERIZATION

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The about 4000 (now maybe 4200) valid mineral species known worldwide (Moon and meteorites included) occur in very various environments and show extremely variable grain or crystal sizes. Some 500 or more mineral species were encountered only under the microscope and a few only as inclusions in other minerals; they are commonly named microminerals. By using more powerful methods it is possible to identify minerals at micrometer or even nanometer scale. Two more categories can be thus proposed, i.e. infra- and nanominerals and the total number of size-related mineral categories increases to four, taking into consideration the macrominerals, the most common and widespread mineral category.

In the world of numbers (multiples and submultiples) the crystal/grain size of minerals can vary between about 10^5 and 10^{-9} mm (Table 1). Outside of this interval mineral grains are unlikely to occur, unless substructures, polysomes etc. as shown by HRTEM could be included in such a systematization. Of course, the mineral species can "migrate" from one category to the others or can exist in all the categories as well. For example, the gold in the shear-zone related ores at Costeşti/Horezu, which has been observed to exist as macro-, micro-, infra- and nanoparticles (Udubasa G. et al., 2006).

Examples can be given for each category of mineral species (Table 2) both taken from literature data and recently obtained by a team of mineralogists and physicists in the frame of a CERES project (C4-2009/2004) supported by the Ministry of Education and Research.

For the category A, macrominerals, i.e. the majority of mineral species (maybe 3000-3500 in number) there have been selected mainly some giant crystals from pegmatites as given by Rösler (1972).

The microminerals (category B) include a relatively large number of minerals, which can be seen only under the microscope and occur mainly as inclusions in other minerals or, by their nature, form only fine to very fine grained aggregates, e.g. clay minerals. Exsolution bodies belong hitherto as well as the daughter minerals in the fluid inclusions.

The inframinerals (category C) cannot be seen nor cannot reasonably good be identified under the optical microscope. They occur either as ultrafine inclusions and/or as very fine intergrowths, a fact preventing a reliable identification as a result of interfering properties.

The nanominerals (category D) cannot be depicted by usual mineralogical/physical methods; even EPMA seems to be useless in many cases. However, their presence can be either predicted (NGR - Nuclear Gamma Resonance) or visualized (TEM/SAED, HRTEM etc.). Namely these nanominerals are the most interesting as they have unexpected properties (as the nanomaterials generally do) and occur also in unexpected environments. In some cases, their formation is not fully understood.

Table 1. The proposed classification/systematization of mineral species according to their size and methods of identification.

General terminology of multiples and submultiples*		Designation of mineral categories	Methods applied for identification
tera / T	10^{12}	Not existing	
giga / G	10^9		
mega / M	10^6		
kilo / k	10^3	Macrominerals $10^5 \dots 10^{-3}$ m	Common mineralogical methods
hecto / h	10^2		
deca / da (dk)	10^1		
deci / d	10^{-1}		
centi / c	10^{-2}		
mili / m	10^{-3}		
micro / μ	10^{-6}	Microminerals $10^{-4} \dots 10^{-6}$ m	Optical microscopy (+ VHN, R%), EPMA, XRD
		Inframinerals $10^{-7} \dots 10^{-8}$ m	EPMA, XRD, NGR
nano / n	10^{-9}	Nanominerals	TEM/SAED, NGR, HRTEM
(angstrom / Å)	10^{-10}	(Ribbons, noduli, etc.)	HRTEM, AEM
pico / p	10^{-12}	Unlikely to occur as mineral species in the common use.	
femto / f	10^{-15}		
atto / a	10^{-18}		

* Marcu & Moga (1978)

Table 2. Examples of mineral categories from the Table 1.

	Category	Range	Examples
A	Macrominerals	$10^5 \dots 10^3$ m	Beryl, 360 t, Malakialina, Madagascar; Phlogopite, 90 t, Lacey miner, Ontario, Canada; Quartz, 70 t, Kazakhstan; Amblygonite, 30 t, Keystone, South Dakota, USA; Topaz, 270 kg, Minas Gerais, Brasil*.
B	Microminerals	$10^{-4} \dots 10^{-6}$ m	Mackinawite, ulvite, isocubanite, matildite, many sulphosalts, daughter minerals in fluid inclusions, clay minerals.
C	Inframinerals	$10^{-7} \dots 10^{-8}$ m	Greenockite, Bi, Au, Bi sulphosalts, schreibersite-like, cobaltite, löllingite, uytenbogaardtite**.
D	Nanominerals	10^{-9} and less	Gold (coral-like aggregates) in pyrite and pyrrhotite at Costești, wüstite and pyroxferroite at Răzoare.

* Selection from a list given by Rössler (1972).

** In gold ores in the South Carpathians (Udubasa S.S. et al., 2006).

Two case studies will be given here:

- (1) The gold ores related to shear-zones in metamorphics of the South Carpathians, i.e. Costești/Horezu, Valea lui Stan/Brezoi and Jidoșțița/Mehedinți. In addition to gold, some inframinerals occur in sulphides in several occurrences; cobaltite and löllingite, mainly included in arsenopyrite, not identified by optical microscopy (surface analysis) but clearly revealed by NGR (volume analysis). Note that both NGR and TEM/SAED analyses were performed on powdered samples, an unexpected advantage in preserving at least the coral-like gold aggregates on sulphide surfaces, which probably would have been probably disappeared by using the ionic thinning of samples. A "by-product" of NGR analysis was the identification of both Fe^{3+} (25.32%) and Fe^{2+} (74.63%) in chalcopyrite from Valea lui Stan, giving this mineral the somewhat uncommon formula of $\text{Cu}^{1+}\text{Cu}^{2+}\text{Fe}^{2+}\text{Fe}^{3+}\text{S}_2$. Some additional data are given in the Table 3.
- (2) The high PT mineral assemblages of the Mn-Fe Răzoare deposit contain some 100 mineral species. The manganoan fayalite (Fe 0.58, Mn 0.36) is a major component of the ores, in association with mangangrunerite, pyroxmangite, manganese bearing humites, etc. The fayalite contains minute inclusions of manganoan ferrosilite (optically presumed and finally identified by XRD) as well as fine inclusions of magnetite (optically) that was proved to exist by NGR and TEM/SAED. In addition, by using these methods wüstite and pyroxferroite were found as nanoinclusions in olivine (Table 4).

Table 3.

Some minerals in gold ores from the South Carpathians.

Size category	Mineral species	Methods used
macro	pyrite, arsenopyrite, galena, chalcopyrite, sphalerite, GOLD.	Observed by naked eyes and OM*.
micro	pyrrhotite, GOLD, Bi	OM
infra	greenockite, GOLD, schreibersite-like, Bi-sulphosalts	EPMA
	uytenbogaardtite	XRD
	cobaltite, löllingite	NGR
nano	GOLD (coral-like aggregates)	TEM/SAED

* Optical microscopy

Table 4.

Some minerals in the Mn-Fe Răzoare deposit.

Size category	Mineral species	Methods used	Remarks
macro	Mn-fayalite,	OM*	Grains up to 20 cm long.
	Mangangrunerite, Magnetite, Manganese humites, Pyroxmangite	OM, XRD	
micro	Jacobsite Magnetite	OM	Inclusions in fayalite.
infra	Magnetite Ferrosilite (Mn)	OM ? XRD	
nano	Magnetite Wüstite Pyroxferroite	NGR TEM/SAED	Inclusions in fayalite.

* Optical microscopy.

Note: Macro- and micro-, partly also infra- (ferrosilite) as given by Udubasa et al. (1996); nano-, see Constantinescu et al. (2004).

Conclusions

A formal, grain/crystal size related systematization of mineral species was already proposed (Udubasa G. et al., 2006) and its refinement is presented here. The mineral categories can be best classified as a function of methods used. The most interesting are the nanominerals. The coral-like aggregates of gold on sulphide grain surfaces is the most

interesting, as it is perhaps for the first time revealed. The TEM/SAED visible gold, some several tens of nm in size may represent an alternative to the invisible gold, proved to be chemically bond in arsenopyrite lattice, as Cathelineau et al. (1989), among the firsts, have shown. The electrochemical processes on sulphides may play an important role in the apparition of such uncommon gold aggregates. Möller et al. (1977) have shown that electrochemical processes can occur on grain boundaries of inhomogeneous sulphides, giving rise to formation of np-junctions, i.e. favourable sites for gold deposition. A further approach is given by Tauson (1999) by using the so-called "gold-assisting elements" such as Cd, As and Se, which can help to enhance the solubility of gold in the gold-bearing systems. In pyrite, Au^{1+} substitutes for Fe^{2+} , that is compensated either by a sulphur vacancy or by a hydrosulphide ion replacing sulphur.

The identification of pyroxferroite (a mineral typical of Lunar samples and meteorites) and especially of wüstite as nanoinclusions in the manganoan fayalite suggests special conditions of the initial metamorphism stages of the Răzoare deposit. Wüstite, practically the first proved terrestrial occurrence in Romania, suggests low to very low $f\text{O}_2$ conditions (the lowest reported so far), probably at the boundary magnetite/native iron in the $f\text{O}_2/f\text{S}_2$ diagram. In addition, the presence of wüstite requires temperatures in excess to 570°C , a fact in agreement with the proposed evolution of the Răzoare deposit (Udubasa et al., 1997).

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**MINERAL DEPOSITS,
GEOCHEMISTRY AND
ENVIRONMENT**

TRANSFORMATION CYCLE OF THE SULPHIDES PHASES FROM THE MINE TAILINGS. CASE STUDY- BAIA MARE AREA

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Explanation from chemical point of view of bonds, has the aim to identify the reactivity and stability of the sulphide minerals from ore deposits from the Baia Mare district which enter the processing, depending on their reactivity and stability in mine tailings.

The covalent bond is present in: PbS, ZnS, FeAsS. Because sulphur has not a high electronegativity, the respective covalent bond will be partially combined with an ionic feature this fact subscribing in a great extend to the reactivity of their compounds.

State more stable, normal conditions of temperature and pressure, with which sulphur will participate to the forming of bonds are those realized with hybrid orbitals. Hybrid orbitals are more stable than the atomic orbitals and interfere on a large part. This condition is not achieved by the pure chemical configuration of sulphur atoms.

To the bonds of sulphides Me_2S_n , sulphur participates as an independent group of type S_2^{2-} . From chemical point of view, these compounds are integrated in the group of polysulphides, because here sulphur forms bonds $(S-S)_n$ due to chain ability like carbon atoms, these chemical elements have not a high electronegativity.

The reactivity of sulphide minerals is explained by the acids – bases theory of Lewis (1923 - fide Nenitescu, 1963). According to the electronic configuration the sulphide minerals are substances with a deficit of electrons. Lewis acids are chemical compounds that have a deficit of electrons in the valence layer. The definition given by Lewis is expanded to the acids and bases field, integrating ionization, complexation reactions; later on, in 1939, Usanovich (fide Nenitescu, 1963) integrates redox reactions as particular cases of acid-base reactions.

After Lewis theory, which classifies acids in 'hard' and 'soft', one can explain the followings:

- the phenomenon of auto-oxidation of Fe_xS_y owes to the reactivity of ions of Fe^{3+} - this being of hard acid (according to the theory of Lewis);
- Lewis intermediate acids: Fe^{2+} , Cu^{2+} ;
- Lewis soft acids: Zn^{2+} , Pb^{2+} - thus explain a lower reactivity of the respective sulphides elements, cover with a oxide protection.

Case study. The district of Baia Mare is one of the most important metallogenetic unit with polymetallic ores, subordinate gold-argentiferous. In this district, there are seven most important ore deposits, from the point of view of contents, namely:

- polymetallic ore deposits, subordinate gold-argentiferous: Ilba, Nistru, Băiuț, Herja, Cavnic – these ore deposits are sources for the extraction of base metals: Pb, Zn, Cu, as well the capitalization of noble metals Au, Ag as by-products;
- gold-argentiferous ore deposits, subordinate polymetallic: Baia Sprie, Șuitor, Săsar - valuable metals obtained are Au, Ag; at Șuitor there are also Pb, Zn, Cu as secondary (Popescu Gh, 1994).

Also, all ore deposits from the district Baia Mare were resource for sulphur.

The mine tailings, tailing ponds "senso stricto" (Pietraru J., 1982), of the jurisdiction of REMIN result from the processing work of ore minerals from Herja, Cavnic, Șuitor mines and those which belong to SC Transgold are resulted from the processing and re-processing of gold ores. From the mineralogical point of view mine tailings are composed of quartz (90%), plus silicates (amphiboles, pyroxenes, clay minerals), carbonates and sulphides consisting of: pyrite, pyrrhotite, marcasite, sphalerite, galena, chalcopirite, as well as iron oxides and metallurgic slags. Solid samples of sterile were chemically and mineralogically investigated for the establishment of the minors tolerated transformations of sulphide minerals and the determination of secondary phases of minerals, stables and unstables. For this study were tested the following mine tailings:

- active mine tailings: Bozânta, Aurul,
- inactive mine tailings: Cavnic I, Cavnic II, Central.

After the **chemicals investigations** of the samples from these tailings by X-ray fluorescence*, the following remarks can be made:

- variation of **aluminium** content; during the phase transformations, feldspars liberate in solution Al^{3+} ions, in exogenous conditions these minerals are completely dissolved; ionic state of aluminium remain stable both at an acid pH and a basic pH, outside of these limits the concentrated solution of Al^{3+} , after the reaction with silicate will form clay minerals.



- variation of **iron** content; the most important step from this cycle is the oxidation of Fe^{2+} to Fe^{3+} , by the atmospheric or dissolved oxygen. Main factors which influence the migration of iron are the presence of O_2 and CO_2 ; $Fe(OH)_3$ and $FeCO_3$ are the common forms of reprecipitation of iron from the solution, but in the presence of other ions, the minors phases can also occur: $SO_4^{2-} \rightarrow PbFe_6(SO_4)_6OH$ – plumbojarosite; $(PO_4)^{3-} \rightarrow PbFe_3(PO_4)_2(OH, H_2O)_6$ – kintoreite; $S_2^{2-}, S_2O_3^{2-} \rightarrow (Fe, Pb)_{12}(S_2)_2S_2O_3$ – viaeneite, all these

minors phases were determined by X-rays diffractometry. Pb appears in all of these minerals because of adsorption phenomenon on oxyhydroxisulphates of iron.

- variation of copper content; after the alteration of sulphur in the copper sulphides it forms minor copper sulphates: $\text{Cu}_2\text{O}(\text{SO}_4)$ – dolerophanite, bornite, covellite, generally, the copper ions pass in to the solution as ions, which concentrate through the adsorption on oxyhydroxisulphates of iron. Such a phenomenon was studied from the first time by Vogt and Rosenqvist (fide Gill R., 1996) who determined the contents $>3,2$ g/t Cu in surficial waters which are passed through mine tailings.

- variation of lead content; galena, which is the main lead mineral from mine tailings, transforms to anglesite; this process is facilitated by pyrite, which forms $\text{Fe}_2(\text{SO}_4)_3$ – this acting like an oxide agent. Sometimes, plumbojarosite forms also by alteration process (Ferguson & Erickson, 1988).

-variation of chromium content; this is a minor element in sulphide minerals, mainly of iron, so it is normal to find a notable concentration (compare with STAS) in mine tailings with intensive transformation; and in this case, it is observed the phenomenon of preferential adsorption on secondary minerals of iron (Vaughan & Craig, 1978).

Microscopy study confirmed observations and suppositions presented above.

Figure 1 – Microscopy photos



a) goethite formed on hematite; N //, x 125



b) goethite formed on chalcopyrite; N //, x 125



c) relicts of pyrite in goethite formed in exogenous conditions; N //, x 125



d) clast of silicate, most possibly amphibole, which have developed goethite on cleavages; N //, x 125



e) clast of slag, which has chalcopyrite transformed on in bornite; N//, x 125



f) goethite formed in exogenous conditions possibly pyrite; goethite formed on pyrrhotite; N//, x 125

The mineral phases identified by our microscopic study of the samples, are similar with the results obtained by Petruian et al. (1959) from the study of hypogene minerals and experimental conditions, thus minerals like calcocite, covellite, anglesite and oxyhydroxisulphates of iron (mineral phase proposed by Petruian is limonite) that can be considered exclusively exogenous, they were obtained in the laboratory. Mineral phases as marcasite and goethite, identified by microscope can be considered secondary minerals, too.

Following mineralogical investigations achieved on actives and inactive mine tailings, we identified next primary also secondary mineral phases: quartz, feldspars, amphiboles, pyroxenes, carbonates, ilvaite, pyrite, pyrrhotite, marcasite, chalcopyrite, sphalerite, galena, hematite, goethite and metallurgical slag.

The main source of secondary minerals consists of silicates and metallic minerals, from the mine tailings. Acid environment, presence of O_2 and the large surface of contact of sterile material from mine tailings, create optimal conditions for transformation of primary minerals in metastable and stable minerals phases. On the base of these results we obtained a scheme of phase transformations (Figure 2) which develop in mine tailings, the main role occupying the sulphide minerals.

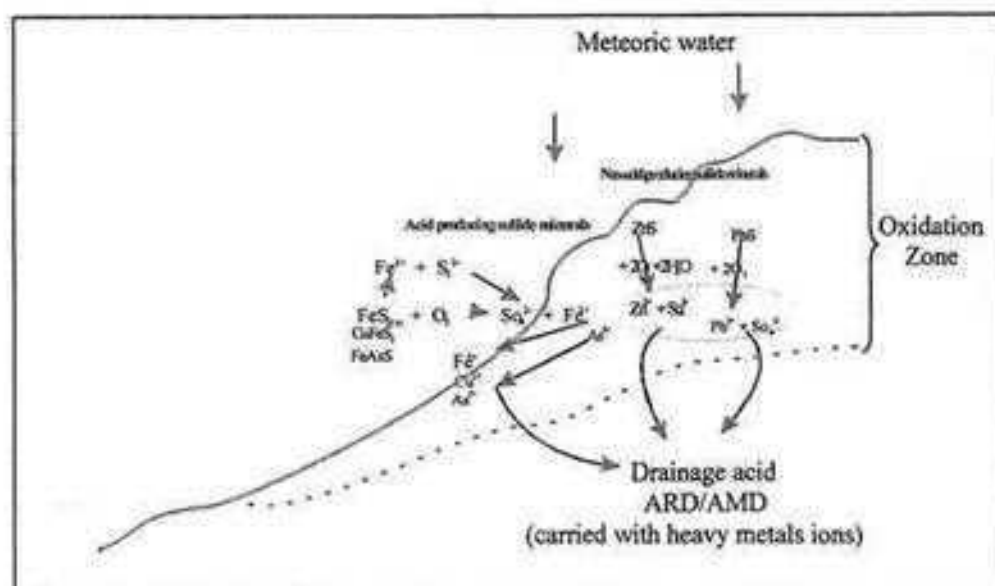


Figure 2 —
of transformation
sulphide minerals
the mine tailings.

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ENVIRONMENTAL RISKS GENERATED BY THE SALT BRINE EXPLOITATION IN OCNA MUREȘ AREA

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The salt massif from Ocna Mureș has been exploited since the Roman times by using some primitive wells. Yet, the first documentary attestation of salt exploitation at Ocna Mureș is dated only as 1695. During the year 1791 at Ocna Mureș the systematic exploitation with wells and bell-shaped rooms started, followed by trapezoidal-shaped rooms. The latter were not used after a while, because of their flooding and breakdown caused by the dissolution of the walls determined by water infiltrations.

Due to the large reserves and the advantageous transport facilities, the Ocna Mureș salt mine - the youngest salt mine in Transylvania, shortly became the most important salt exploitation in the region. The “Solvay” soda factory opened in 1895 that used salt water (brine) as the main raw material underpinned the need for using new methods of salt exploitation: dissolution of saltrock beds. Beginning with 1918-1919, in the context in which the infiltrations that took place in the abandoned mines could not be kept under control, it was decided that brine to be produced by pumping water into the well of the Iosif mine. This water was collected into a big underground tank (at level 170) and then pumped to the surface inside the premises of the “Solvay” factory. Due to the increase of necessary amounts of brine as industrial raw material, a field of surface drills was opened in 1953, reaching the depth of 1060 m. The last stage of development was reached between 1987-1989, by the drilling of five new boreholes located in the Războieni mining field. The exploitation of solid salt ended in 1978.

The salt ore from Ocna Mureș was the first one in Romania where the new method of salt exploitation as brines obtained by drilling was applied: in 1929 at Ocna Mureș the salt extraction as brines was performed by the method of static dissolution, while starting with 1954, for the first time in the world, the new method known as kinetic dissolution (patent owned by Eng. Dima) was introduced. Thus, three drilling fields were active, two starting from the surface until 1100 – 1700 m depth and another one starting with the –110 m horizon. Since 1978, salt was exploited only by drillings, from both ore deposits in Ocna Mureș and Războieni.

From a geological point of view, the Ocna Mures ore deposit belongs to the Neogene zone of the diapire folds from the south-western part of Transylvania. The deposits are of a

Neogene (Badenian, Sarmatian, and Pannonian), and of a Quaternary age. The salt shows regressive feature and is assigned lithostratigraphically to the Ocna Dej Formation (Middle Badenian = Wielician). The ore crops out in the central part of the Ocna Mures town, as a diapir about 900 m in length and 500 m in width, with the root located at a depth of 1200 – 1400 m.

Tectonically, the Ocna Mureş region, situated on the western border of Transylvania is part of an intensely folded area, consisting of a series of closely packed anticlines and synclines. Due to the fact that no geological deposits are currently overlying the salt deposit, it is considered that the diapirism phenomenon is still continuing at present with an intensity that depends on the indirect pressures, lithostatic pressures and on the specific plasticity of salt the massif is build up.

The regional geological research evidenced the presence of an N 70°-80° E oriented fault about 20 km in length located beneath the Mureş valley, parallel to the direction of the river bed (the "Mureş' fault").

From a mineralogical point of view, the deposits can be considered as being monomineralic, halite representing 96-99 % of the total rock weight.

The environmental risks generated by the presence of salt in this area are connected to the old mining works, but they are also controlled by the anthropic factor. For this reason, all the hazard factors induced by the presence of salt have to be considered, and in the same time the saliferous areas in general, but in particular the Ocna Mureş area, have to be carefully and continuously monitored.

One of the risks in this area is bound to the multiple effects of salt solubility in the Ocna Mureş salt ore. The direct contact of salt with waters from aquifers located in the area of the ore deposit lead to the development of superficial karst phenomena at the top of the salt bed; as a result of the collapse of the overlaying alluvia, a large groove formed. This collapse channel covers the area of occurrence of the salt ore, as well as an important part of the adjacent area.

In time, due to the establishment of hydraulic connection between the voids represented by the old mining works and the aquifer, intense dissolution processes determined the collapse of several mines with effects that propagated up to the surface, reinforcing the amplitude of the groove.

Starting with 1978, complex studies were carried on in the area, as well as specific projects and programs designed to limit at maximum the processes of collapse and subsidence of the salt ore affecting the salt massif and the adjacent constructions. The results have shown that the subsidence process is slow and continuous on large surfaces, but without sudden

variations that could endanger the integrity of the civil buildings situated in the regions nearby the salt massif.

Mureş River has a significant influence on the salt ore, as a source of water supply for the phreatic horizon. The circulation of freshwater determines at the surface of the massif the intensification of dissolution processes. Additionally, historical records show that the river waters flooded three times (1818, 1860, 1913) the old mines.

At present the underground works in the Ocna Mures ore deposit are all flooded. Inside the salt massif the water circulation is reduced and it is activated only by differences in salinity vertical gradients, by freshwater infiltration through the drillings that are not perfectly sealed anymore.

The exploitation of the salt from Ocna Mures leading to the formation of voids inside the massif produced deformations of the land surface, emphasizing the depressionary feature of the region. The internal crumbling and collapses that followed and that extended up to the surface created the favourable conditions for the genesis of some lakes. These lakes formed artificially within the crumbling sinkholes from the surface, resulted by the collapse of the roofs and pillars of the old mining cavities. The crumbling phenomenon progressed in time beginning with 1791 when the systematic mining started, and it gradually became hazardous until to 1954 when it was decided to perform hydraulic rambling of the old mines. The hydraulic rambling, finished in 1958, resulted in the formation of the salt lakes at the surface. Since their formation and up to the present, the lakes continuously changed their shape, surface and depth extension. After 1978 the processes of crumbling, with effects up to the surface have stabilized and at present, the subsidence is constant.

Another factor of risk that one must take into account in this area is the presence of the two tailing ponds (Rom: "batale") created on the left side of Mureş river by the Chlorosodic Products Plant in Ocna Mureş in which the waste resulted from natron processing was deposited. These occupy a large surface of land, about 160 ha on both sides of Mureş. The solutions released from the industrial processes were transported to these ponds through a system of pipes. The large volume of liquid stocked in these places, distributed on large surfaces can be at any time a source of severe pollution for the Mureş River. A part of these "poisons" is periodically transported by rains or winds across the arable lands as well as into the water of the rivers. Some of them are constantly flowing into the waters of Mureş through some gutters that are located around the ponds. Besides the solutions deposited in the ponds, there are also big amounts of solid saliferous products stored next to the Mureş River. There are high risks that they get into the Mureş waters and produce a severe pollution during the rainy periods when the river floods the banks.

Also, another factor of risk can be considered the Chlorosodic Products Plant itself. The measurements made in 1997 by ICIM Bucharest on the quality of the air in Ocna Mures, seriously influenced by the emanations of this plant, showed pH values of 6.5. This pH determines the formation acid rains in the region whose erosional effect on the buildings and metallic equipment is well known.

In order to diminish all the above mentioned risk factors, specific measures have to be taken, such as: proofing and hydroisolation of the platforms around the mining wells, in order to prevent the infiltration of waters from the Mureş River and the rain waters. In the same time it is important to build collecting channels along the banks of Mureş River, in order for the brines resulted from saliferous waste to be deposited and discharged into a system of ponds for preventing further risks in the area. Further desalination of these brines could make possible their depletion into the Mureş River.

Conclusions

The Ocna Mureş salt ore is characterized by very difficult hydrogeological conditions that requested significant measures to be taken for regional protection starting with the XIXth century. The long-term risks affecting the salt massif were related to the waters of the Mureş River and to the infiltration waters from the Banţa Hill, situated next to the salt ore. In order to prevent a new flooding of the old mines (like those three events mentioned above), the waters of the Mureş River were re-directed into an artificial bed created at about 400 m north from the salt massif; between the two river flows an earthy dam was built.

Subsequently a partial solution was found for preventing the water infiltration represented by building of a 14 m deep drainage channel through the barren rocks, at about 15 m away from the massif, whose effect was immediate.

In time, in order to protect the deposits against uncontrolled dissolution and surface degradation related to underground infiltrations, it was necessary to apply the hydraulic rambling of the voids with concentrated salt water, underground cementing with solid impermeable materials or protecting liquids. However, all these actions did not have the expected results because of the intense water circulation and the large amount of fresh water in the lakes on the top of the salt deposit.

**THE Cd, Cr AND Co POLLUTION IMPACT IN THE PAÍNS - CÔRREGO
FUNDO, PROVINCE PAÍNS - ARCOS - DORESÓPOLIS, MINAS GERAIS,
BRAZIL**

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Introduction

The Carstic Province of Arco-Paíns-Doresópolis is located in the area of upper San Francisco region, in the Southwest of the Minas Gerais State (*fig. 1*). The Riacho Fundo-Paíns characterized by exposition of calcareous / dolomitic rocks and an exuberant vegetation (Radambrasil, 1983). An intense exploratory activity of carbonates rocks was developed and contributes to the economy of the area since the beginning of the 60's.

The "ravine" or "craft" ovens are built in slopes in the land, taking advantage by the level differences, in the way to build a base where is possible to put in the incinerate materials and on the top where it is possible to put the limestone fragments. This area is considered as one of the largest producing of whitewash of the State. The proprietors of the ovens, at least till 20 years, began to use for it burns of the limestone, residual oils, erasers, tires, aluminized paper, plastic residues, among other, that represented the discard of industrial garbage of great companies from São Paulo and Minas Gerais States. This incineration of industrial residues generates gaseous and solid emissions, together with the products of an incomplete combustion formed during the process of it burns with lack of oxygen (Fergusson, 1991), which caused an increment of pollutant in the atmosphere and, after the precipitation, in the soil, the water and the vegetation (Brigden *et al.*, 2000).

Geological setting

In the area of the work crops out the basic Granite-Gneiss Complex and rocks of the carbonate and pelite sequences of the Subgroup Paraopeba, Bambuí Group. Banded gneisses predominant of granites composition, medium granulation, often deep weathered form the Granite-Gneiss Complex. The gneisses have incipient banding of whitish gray parts with rosy (alkali-feldspar). Besides this orthoclase exist plagioclase, quartz, biotite, and subordinated microcline, muscovite and chlorite. The Paraopeba subgroup, Bambuí group, was represented

by two different facies, a pelitic and a carbonate. The pelitic facies includes terrigen (meta clay and laminated meta-siltites) rocks. Occurs stratified intercalated dark carbonate sheets of fine granulometry in advanced diagenesis or incipient metamorphism. The rocks are deposited in no conformity, directly on the gneisses or of them separate by lenses of lithic conglomerate. The carbonate facies is constituted by a great variety of calcareous and dolomites rocks. They are characterized by the abundance of allo- chemistry and microbial activities, together with little orto-chemistry rocks and impure sediments like impure carbonates and loamy terrigenes. The winds are of two predominant directions (NE and SE). The orientations of the valleys modify these preferential directions locally.

Three types of soils basically, according to their likeness limestone – Podzol ; Pelitic – latosols and c. Granite-gneissic - latosols.



Fig.1. Regional map of the location of the investigated area within the Project "Provincia Cárstica Arcos-Pains-Doresópolis". Visible is the location in upper Rio São Francisco region.

Methods

The samples were removed in a grid of 500 X 500 meters in the sense N-S and E-W, including total of 2.700 hectares. 120 samples were collected. The samples were removed of the superficial horizon of the soil (<10cm). Separate from the organic materials the soil appears to be clay and homogeneous. Each sample was removed following the same procedure: a. Taking of material always from the same superficial area (100 cm²); b. Collection of 1kg of soil and the stockage in plastic bag; c. Description of the main parameters found in the field. The samples were transported in the plastic sacks and conditioned inside of dark boxes by lower temperatures. The analyses were executed on a wd - FRX Siemens SRS 3000.

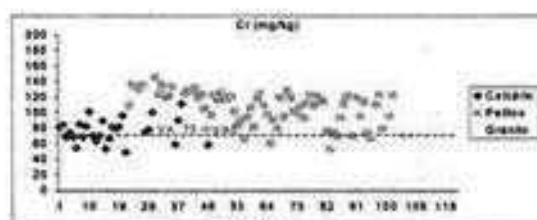
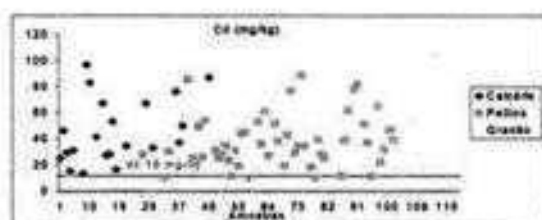


Fig.2. Distribution of Cd and Cr contents in comparison with the intervention values (VI) and alert (VA).

Geochemistry

The great part of samples has the Cd, Cr and Co content higher than the values published by CETESB (2001) representing risks to the human health (Alloway & Ayres, 1994).

The highest values of Ba happen preferentially on the soils under granite substratum and also in the area of the contact with the metapelites and the smallest concentrations in formed soils of metapelites and limestones. The Pb present a quite homogeneous distribution about the 30-mg/kg lowers to alert value (VA) published by CETESB (2001). The Cu, Ni and Zn content are extremely homogeneous respectively around 36-mg/kg, 15-mg/kg and 78 mg/kg very weak comparatively to values of CETESB (2001) near the 300-mg/kg. The presence of oxides and hydroxides of Fe, Al and Mn in the soils interferes in the fixation of heavy metals (Alloway & Ayres, 1994). The Fe_2O_3 and Al_2O_3 have a positive correlation with Cr, Co and Pb content, light positive correlation with Ni and As and negative correlation with Zn and Ba but the Cd doesn't show any relationship with Fe_2O_3 and Al_2O_3 .

The chemistry distribution maps (fig.3) show the distribution of the selected metals in the superficial part of the investigated area together with the location of the sampling points, the plants, the quarries and the ovens.

The Cd content presetting a homogeneous distribution and doesn't show correlation with different lithologies that it composes a substratum. The highest concentrations are located in proximities of a plant and calcinations ovens at a most to 500 meters and in areas with high topographical quotas. The distribution of a Cr contents is similar to Co and Pb content. The heavy metal concentrates proximities of a craft and industrial ovens and on top of pelitic rocks. A highest tenors are localized near (300 or 400 m) of an ovens direction of a wind; height of a chimneys.

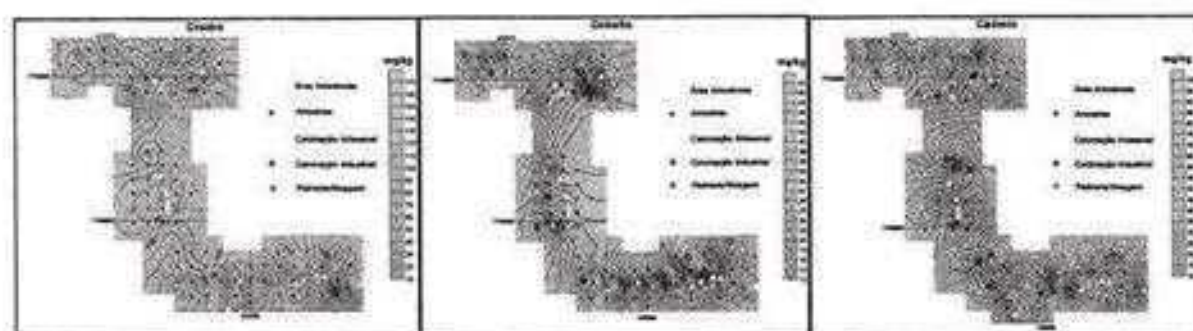


Fig.3. Map of Cd, Co and Cr distribution in the soil of Arco-Pains-Doresópolis province.

Environmental impact factors

Factor of Contamination (FC) is a ratio between the concentration of a metal in the sampled sediment and the natural concentration or background of a defined element. The Index of Geo-accumulation (I_{Geo}) is a quantitative measure of a pollution caused by heavy metals (Laybauer, 1995).

The factors of contamination of Cd, Co, Cr and Ba, ($FC_{Cd} = 100$ and $FC_{Ba} = 18$) are very higher preferentially on soils built over the granitic and pelitic substratum but always in the proximities of mining and calcinations activities. The Ni, Pb and Cu factors contamination are low values and the FC_{Zn} (12) is slightly higher of these probably reflecting primary concentrations in lithologies.

The I_{Geo} of Cd presents medium and punctual high values that represent soils of strong to very high pollution ($I_{Geo} > 4$). These concentrations are distributed preferentially in the proximities of calcinations activities and in points of high topography, indicating a transport and distribution of cadmium by wind and rain and an entropic origin for the anomalous presence. The Cr, Co, Cu and Zn show a punctual enrichment reflecting a considerable pollution degree ($I_{Geo} 1 < 3$) in this area.

Conclusions

The high pollution in heavy metal is localized in the proximities of the plants and the calcinations ovens; principally for Cd, Co, Cr, Ni and Pb and smaller degree for a Ba, Zn and As (using FC and I_{Geo}). The wind is a mean transport of heavy metal pollution distribution. The highest concentrations of Zn are in proximities of rural properties (agronomy) and over the Bambuí limestone formations.

The burn of plastic materials and other chemical products, like chips of rubber, aluminized paper, residual oils etc. is considered the principal source for the high concentrations of Cd found in soils.

Acknowledgement

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GEOCHEMISTRY OF SEDIMENTS FROM AMAZONIAN RIVER AND HIS AFFLUENT BETWEEN MANAUS AND BELÉM

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Introduction:

The Amazonian Basin, formed from a diversified system of great rivers, occupies an area of 6.100.000 approximately Km² and its rivers carry a vast volume of water and sediments varying with the stations between 60 and 280x10³ m³/s. The conditions of the humid tropical forest with its high rainfall contribute so that the rocks that arise in the Amazonian Basin suffer an intense process from chemical and physical weathering. In the last few decades an enormous amount of agricultural and industrial activities occurred in the Amazonian area. During 2000 October, we participate of the route of the Humboldt Expedition – Amazonian. We present information of the state of sediment and water in Amazonian river between MANAUS and BELEM.

Geological setting:

The underground of the Amazonian Basin is formed by a wide variety of rocks with different ages. In a general way it is possible, to divide the Amazonian Basin by its physiographic characteristics in a lowered central main valley tacked at the flanks north, south and west by topographical highs. Along the central gutter of the Basin, concordant to Amazonian river, rocks of Paleozoic age crops out, mainly of sedimentary origin, deposited by transport processes in sea-environment, and of Mesozoic age deposited in continental surroundings. The Basin is limited to the north and the south by a Pre-Cambrian crystalline basement belonging to the Guyana of and of Central Brazil Shields. These units are composed by granites, gneisses, volcanic acid and basic rocks and older meta-sedimentary deposits (DNPM, 1993; Vital & Stattegger, 2000). At the western limit of this Basin a great variety of rocks units belonging to the Andean and pre-Andean region can be found. Volcanic acid and intermediate, shales, limestones and sandstones, together with rocks of Mesozoic and Cenozoic ages, compose these units.

In the Basin, the higher parts are covered by red and yellow lato-soils and podzolic soils. Close to the Amazonian River main valley and at the margins of their largest tributaries it is

found type gley alluvial soil, together with portions of litolic soils. Close to the ocean, in the eastern portion of the estuary, lateritic hydromorphic horizons and saline soils due to the influence of the tide can be found.

Materials and Methods:

The sampling itinerary is part of the route of the Humboldt Expedition - Amazonian 2000, during October, month with normally low rain that guarantees low water levels, easy access to the sediment and higher contaminant contribution due to lower dilution and the of liberation - fixation chemical processes determine the element concentrations. Figure 1 show the sampling points, selected in function of possible significant heavy metal contaminations by human activities. 20 samples sediment were taken from the principal stream and near the inflow of the principal contributors, between MANAUS and BELÉM DO PARA and in the northern part of Amapá State.

At each collecting point, the principal physical properties also were taken. For 1-2kg sediment samples were collected at the margin of the river, conditioned in bags of non-reactive plastic, frozen and transported to Belo Horizonte.

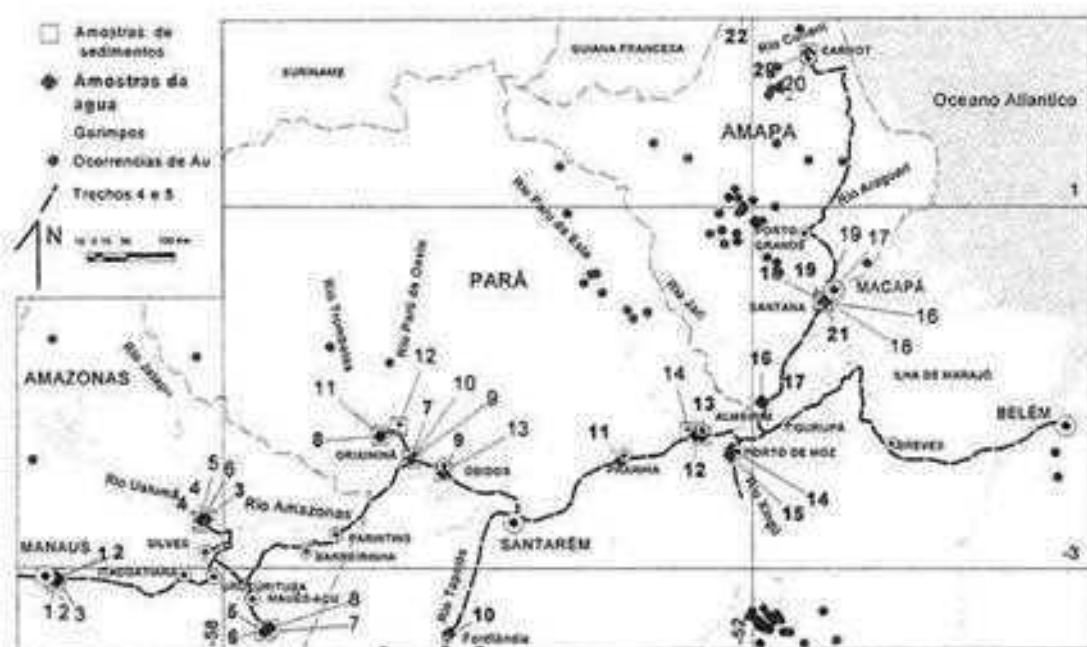


Figure 1: Location map of the sampling points for of sediments and of water. The map also shows the main contributing rivers and cities as well as the location of some digging activities.

Sediments:

We classified the samples by locality and affluent of Amazonian at end of better apprehended the local geochemical problem and to distinguish them from the general

evolution of the sediments of the Amazonian area. The whole of the samples are distributed between the sandstone rich in silica and those rich in clays. We have constant a $K/Na+Ca$ ratio thus showing a strong magmatic component of these sediments, except for sample 1 and 2 near MANAUS city where shows anthropogenic activities Calcareous rock mining in the river Jatapú and sample 7 near ORIXIMINA.

The sedimentary sorting involves a fractionation between the very aluminous sediments and whose composition tends towards pole Al, the shales and of the sediments rich in quartz and feldspar, the sandstones (figure 2). The major elements of the sandstones are not very variable, which makes it possible to show a weak variation from the proportions from the principal mineral phases.

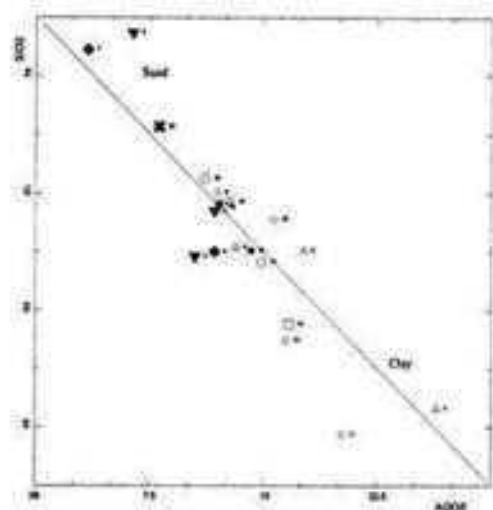


Fig. 2

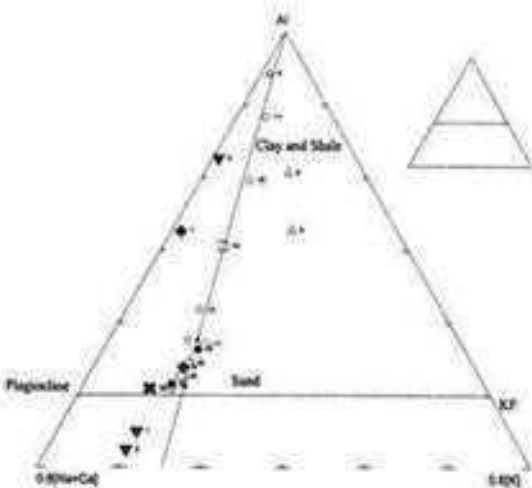


Fig. 3.a

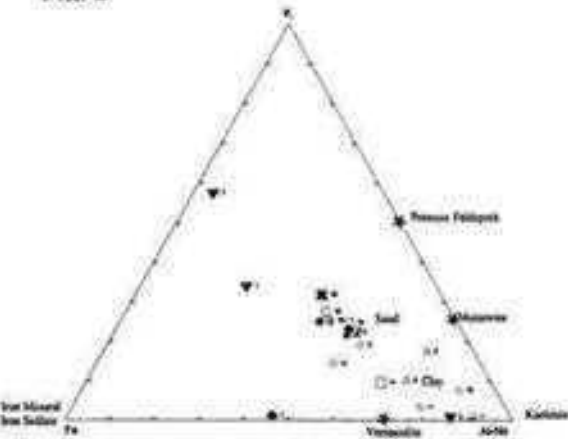


Fig. 3.b

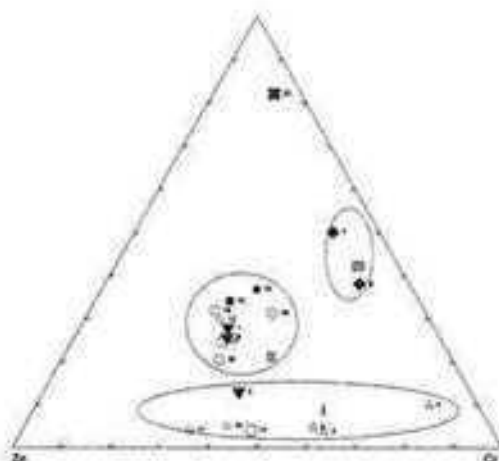


Fig. 4

Figure 2: Distribution of sediments from Amazonian river and his affluent in SiO_2 versus Al_2O_3 diagram.

Figure 3: Distribution of sediments from Amazonian river and his affluent in (a) Al-K-(Ca+Na) cationic diagram and (b) K-(Al-Na)-Fe cationic diagram.

Figure 4: Zn, Cr and Cd contents distribution of sediments from Amazonian river and his affluent.

The samples 10 and 11 from ORIXIMINA city and samples 4, 5 and 6 from Rio Uatuma have a very marked clay component. However, same samples 9, 10 and 11 from ORIXIMINA and samples 15, 16, 17 18 and 19 from SANTANA and MACAPA cities have a clastic (quartz, feldspar and micas) component important. They are probably resulting from the sedimentary sorting and the weathering of Precambrian and Palaeozoic substrate that the affluent Rio Uatuma, Rio Trombetas and Rio Paru are crossing in the east.

The heavy metals Cr, Zn, Co, Cu and Cd of the sediments from Amazonian river are generally with the top of the normal limits given by the organizations of environmental protection (Alloway & Ayres, 1994). They are linked to the mining activity that develops in the area. The Zn and Cr contents are much more enriched in the argillaceous components; on the other hand the samples characterized by an aluminous clastic fraction are richer in Cd (figure 4). Samples 7 and 8 are low in Zn compared to the other samples. These variations are also in relation to a strong mining activity in MACAPA and CARNOT, gold mine.

Conclusion:

The geochemical data of sediments from Amazonian river and his affluent suggests an important sedimentary sorting and the weathering of Precambrian and Palaeozoic substratum in evolution of these sediments.

The heavy metals Cr, Zn, Co, Cu and Cd of the sediments from Amazonian river are generally over alert value published in literature. The Zn and Cr are much enriched in the argillaceous components and a few sediments samples rich in Cd characterized by an aluminous clastic fraction. This pollution is linked to the mining activity in the Amazonian area. However, the heavy metals in the water are very low.

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PORPHYRY COPPER MINERALISATION FROM BOLCANA, METALIFERI MTS; PETROCHEMICAL AND GEOCHEMICAL ASPECTS

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The Bolcana porphyry copper ore deposit is located in the SW part of the Brad-Sacaramb metallogenetic District, at approximately 15 Km from Deva town. The copper-gold mineralisation has a spatial and genetically relationship with a subvolcanic body, formed of amphibole-bearing andesites/microdiorites, named Bolcana andesite. The Bolcana ore deposit is located in the central part of the Troita-Magura metallogenetic knot (Brad-Sacaramb district). This metallogenetic knot is characterized by a large occurrence of a mineralised structures in the small area (aprox. 8 Km²) (fig.1). Several base metal and Au-Ag veins and veins system which cross the Neogene volcanic bodies (rarely ophiolitic basement) developed around the Bolcana structure form a "ring-zoning mineralisation related to caldera structure" (Popescu & Neacsu, 2005).

Cioflica et al. (1966), before the Bolcana was discovered, remarked a concentric disposition of the mineralizations, the Pb-Zn one in the inner part and Au-Ag mineralisations in the outer part. 3D GEOCAD modelling indicate the homogeneous 3D zonality of the Au and Pb-Zn deposits centered on the porphyry; Pb-Zn deposits are closer to the porphyry and located deeper compared to the Au veins which are more distant from the porphyry and closer to the surface (Cardon et al, 2004) (fig. 1).

The ore deposit has been investigated with mining works (at five levels) and drillings works spanning over 1200 m in depth. The Bolcana subvolcano has an elliptic shape, with a maximum size (750 x 450 m) at Grimm horizon (+330 m) and decrease towards upper horizons (150 x 100 m). It intrudes the ophiolitic basement (J), the Almasu Mare sedimentary formation (Pg1) and Neogene andesitic lava flows (Faerag-Hondol andesites). Its emplacement was accompanied by breccification and an external heterogeneous breccia halo (~ 50 m) is present. Post-emplacement fractures (with NS orientation) cross the subvolcanic structure. The explorations have made possible to outline four cylindrical breccia columns within the Bolcana subvolcano ("breccia pipe") which were richer in mineralization (the F17, F282-F13, F21-F4 and F3 zones).

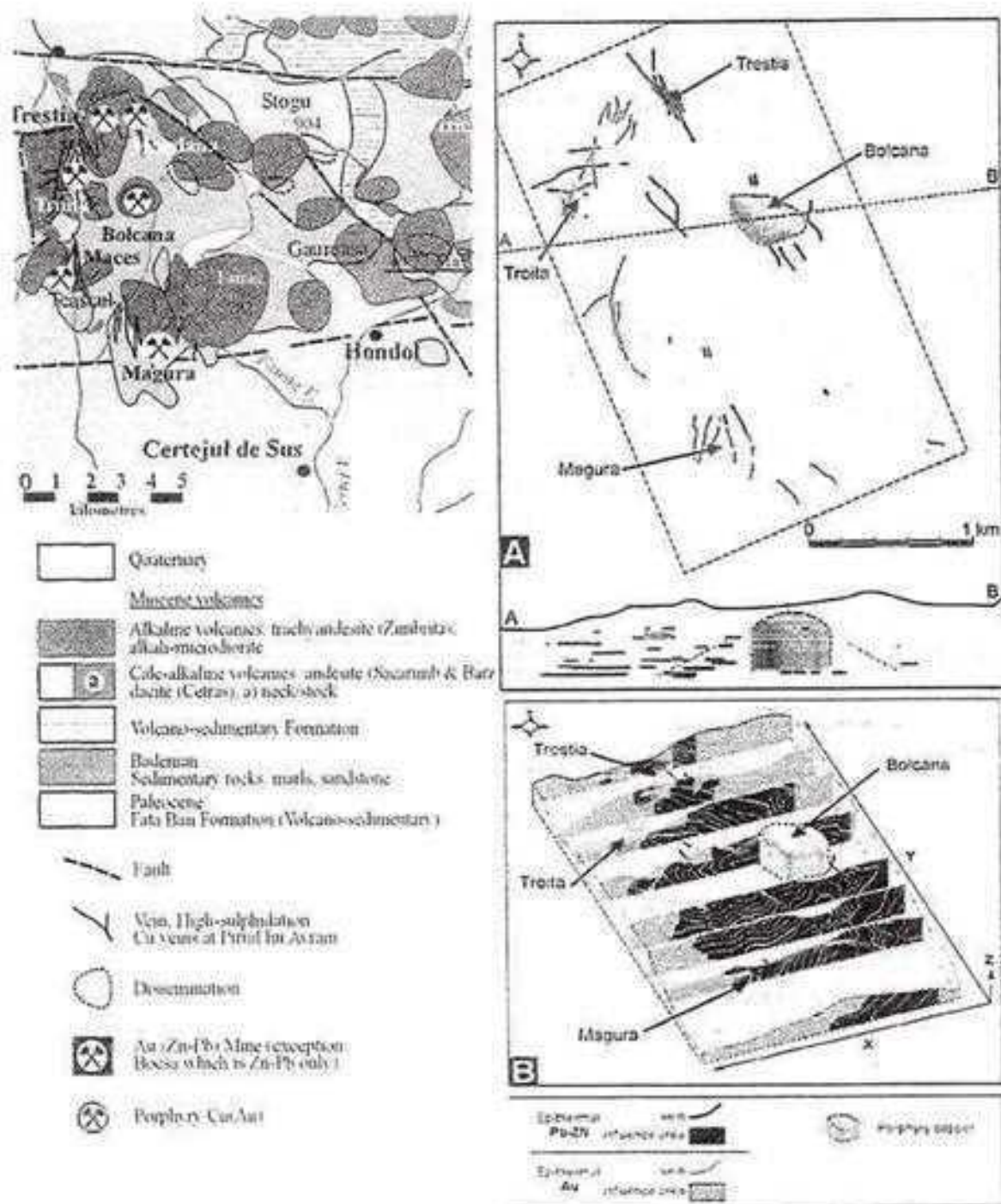


Fig. 1. In the left: The geological map of Bolcana area and deposit locations; compiled from Ghitulescu and Socolescu (1941), Udubasa et al. (1992); the „Geological map of South Apuseni Mts, Alpine and Magmatism and related Ore Deposits (IGR, 2001) in Ciobanu et al., 2004; in the right: geometric deposit modelling with GEOCAD software. (A) Horizontal plane and horizontal projection in a vertical AB plane of the porphyry of Bolcana. (B) Au and Pb-Zn zonation represented in a prospect plan obtained by software interpolation, in Cardon et al, 2005

Hydrothermal mineralisations and alterations: Bolcana structure is characterized by the association of the two types of mineralizations: (1) *the porphyry copper mineralization type* with chalcopyrite – magnetite (hematite) - pyrite ± bornite ± molybdenite ± native gold (mainly as inclusion in the chalcopyrite) occurring in the central part of the ore deposit; as microveins forming stockwerk and impregnations, superimposed on a potassic alteration

zone; and pyrite $\pm$ chalcopyrite (covellite) $\pm$ magnetite(hematite), dominant towards the upper and marginal part of the intensely argillized mineralized body; (2) *the low-sulfidation epithermal mineralization* (sphalerite - galena - pyrite - chalcopyrite - tetrahedrite - bourmonite - marcasite - pyrrhotite - native gold) like veins. Four alteration types were distinguished: potassic, phyllic (less developed), argillic and propylitic. The alterations assemblages are typical for porphyry ore deposit, but are noted also superposing of these, showing a complex evolution of the hydrothermal process at Bolcana. Around the epithermal veins, a phyllic and argillic alterations are recognized (Milu V et al, 2003). A large development of sulfidation (anhydrite) and carbonatation (calcite) is a peculiarity of Bolcana (Udubasa G, 1981 in Milu V et al 2003).

Geochemistry Major and trace elements content was analyzed by MINEXFOR SA, using spectroscopy and polarographic methods. Bolcana andesite is characterized by 57-63% SiO₂, 0,8-1,9% K₂O and 3.25-3.31% Na₂O, *which enlists it* in the field of calc-alkaline andesitic type rocks. A limited number of trace elements (Co, Cu, Zr, Y, Mo, Sc, Ti, Mn, V, Ni, Zn, Pb, La, Ga, Sn, Ba, Sr) were analyzed in global samples from Bolcana ore deposit. LILE, especially Sr and Ba are counting relatively high values (in average 600 ppm, respectively 400 ppm in fresh rocks from Bolcana subvolcano) with a very large variations in this structure. This aspect is observed in the whole volcanic area from Metaliferi Mts, especially for the rocks younger than 12 Ma. Besides, a high Sr/Y report *enlists* those rocks near adakitic field defined by Defant and Drummond (1990) (Rosu et al., 2004). Some geochemical characteristics give the Bolcana andesites an adakitic-like features (SiO₂ $\geq$ 56% , Al₂O₃ $\geq$ 15%, MgO <3%, Sr >300 ppm, Y<15 ppm). On the Sr/Y vs. Y diagram, Bolcana is placed near the adakitic field. A small values of Sr/Y may be influenced by hydrothermal alterations. Many giant porphyry copper ore deposits are associated with adakites -like rocks.

Following the distribution of metallic elements in the ore deposit and their behavior in the two types of mineralisations (the porphyry copper and the epithermal type) it's clear that:

In the porphyry type mineralisation, Cu and Au (probably also Ag) increase with the depth, while Pb and Zn have an opposite behavior and decrease, the highest values being at the top of the subvolcanic structure. In this case, Au is linked mostly with the sulphides (as inclusions in chalcopyrite, bornite, pyrite). Between Cu and Au, Ag a positive correlation exists. In the veins mineralisation, Au and Ag have a positive correlation with Cu, but negative one with Pb and Zn. This fact could suggest that this metals come from (have origins in) different sources (zones).

The vertical zonality of mineralisation in the ore deposit is doubled also by a regional zonality, spatial superposition of those two types of mineralisations, and also circular disposition of volcanic body and vein systems around Bolcana subvolcanic body is explained by a multistadial evolution of a calderanean type volcano-magmatic complex system who developed the so named „ring-zoning” of copper, polymetallic and gold-silver mineralisations. This model was proposed by Popescu and Neacsu (2005, 2006) to explain the relationship between Cu-Au and polymetallic metallogenesis in the other areas with similar structures, like Rosia Montana-Rosia Poieni, Musariu-Bradisor, Valea Morii-Ruda, from the Apuseni Mts.

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ENVIRONMENTAL IMPACT OF VĂRATEC MINE, BĂIUȚ REGION (MARAMUREȘ) ON SURFACE WATERS

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Introduction

Văratec ore deposit is part of the Băiuț – Văratec – Poiana Botizei metallogenetic field, located in the eastern end of the Oaș – Gutâi volcanic chain in the East Carpathians. The systematic geological study started only in the XIXth century, however the mineralised structures were mined for centuries, providing one of the main economic activities in the region. Starting January 1st 2007, the Romanian government will not offer any financial subsidies for the uneconomic mining activities, therefore the Văratec mine will be closed. In this chain of events, the environmental impact of mine represents one of the major issue of closing process.

Geological background

The metallogenetic processes leading to the formation of the Văratec ore deposits are closely connected to the evolution of the Upper Tertiary intermediary calc-alkaline magmatic regional events in the Gutâi Mountains (Borcoș, 1994). The magmatic rocks in the Băiuț – Văratec – Poiana Botizei metallogenetic field were generated during the second, Pannonian volcanic cycle (Kovacs et al., 1997) in the Gutâi Mountains. The corresponding ore deposits were formed during the third metallogenetic phase, being associated to pyroxenic andesites.

The geology of the area relates to Jurassic, Cretaceous and Paleogene sedimentary formations included in the Pienid units, post-tectogenetic Neogene and Quaternary sedimentary deposits as well as explosive, effusive and intrusive volcanic sequences. The complex tectonic pattern resulted from the movements leading to the formation of the Pienid Nappes, followed by the reactivation of previously-formed faults and the formation of new ones, synchronous with the magmatism (Borcoș & Gheorghită, 1976).

Ore deposit description

The sedimentary formations in Văratec area are Eocene, Badenian, Sarmatian, Pannonian and Quaternary in age. The magmatic processes lead to the formation of explosive, effusive and intrusive rocks. Hornfelses resulted at the contact between the subvolcanic bodies and the sedimentary rocks, while hydrothermal alterations represent the effect of postmagmatic fluids on the surrounding rocks. The Eocene and Neogene formations build up a monoclinic structure, the former locally showing tight bending. Explosive volcanic

sequences, followed by effusive rocks resulted from lava crystallisation occur at the top of the various sedimentary units. The ENE-WSW – oriented fractures were formed prior to the volcanic activity, while the NE-SW fractures – typical for the upper parts of the ore deposits – were subsequent to it (Borcoş et al, 1977).

Văratec ore deposit consists of 18 NW-SE – oriented veins. Three groups can be defined: north-western (TransLivia, Livia, Văratec, Radu – Vasile, Gheorghe, Ramură Livia and Maria veins), central (Ioan Vechi, Ioan Nou, Tereza, Alexandru and 200 veins), and south-eastern (350, Botiza II, Botiza I, Botiza III, Botiza IV and Borcut veins) ones. The veins belong to three fracture systems: NE-SW, ENE-WSW and NNE-SSW. Their length varies between 0.2 km and 5.9 km, with an average of 0.9-1.5 km. The vein thickness varies between 0.2-0.3 to more than 5.5 m. The current height of the mineralised level is variable, from tens of meters in the case of less-developed veins, up to about 500 m. The veins show diverse textures, most frequently being present the banded, brecciated, massive, cockade and geode ones; impregnations occur subordinately.

Mineralogy and geochemistry

The veins in all the three vein groups of the Văratec ore deposit are almost mineralogically identical, the differences being related to the ratios between the mineral species. The following mineral classes are represented: native elements, sulfides, sulfosalts, wolframates, oxides and hydroxides, carbonates, sulfates and silicates (Costin, 2005). Among the native elements, gold shows similar compositions throughout the deposit.

Quantitatively, sulfides dominate: the most frequent species are pyrite, chalcopyrite, sphalerite, and galena. Marcasite, pyrrhotite, arsenopyrite, bornite, chalcocite, covellite and bismuthinite are subordinate. Even if sulfosalts occur in considerably lesser amounts, they constitute an essential part of the mineralization. The most frequent sulfosalts are terms of the tetrahedrite – tennantite series; bourmonite is subordinate, while terms of polybasite – pearceite series are sporadic. The presence of bismuth sulfosalts is a characteristic feature of the veins from Văratec. The chemical data showed the presence of some terms from the lillianite – gustavite series, of matildite, pavonite, berryite and wittichenite.

Another typical mineralogical aspect of Văratec ore deposit is the presence of wolframates. This class is represented by wolframite – the Fe-rich term (ferberite). Among oxides, hematite and magnetite were identified, while hydroxides are represented by lepidocrocite and goethite.

Quartz is the most widespread barren mineral in the veins from Văratec. It shows various colours: greyish-white, dark grey or smoky, violaceous or transparent. Carbonates are mainly represented by siderite and calcite, rarely by malachite and cerussite. Sulfates are

scarce, among which gypsum, barite and rarely anglesite were noticed. Clay minerals occur as nests in the central parts of the veins.

Geochemically, the Văratec ore deposit belongs to the polymetallic type (Pb, Zn, Cu) with significant contents of precious metals (Au, Ag). The veins in the north-western group are dominantly Cu-rich, while the veins in the central and south-eastern groups are Pb-Zn-rich. The veins in the north-western and central groups are dominated by W and Bi, while the south-eastern group is characterised by Cd and Sb. Pyrite and marcasite are rich in As, Co, and partly Ni and Ag. Relatively high contents of Ag and Bi were noticed in chalcopyrite, especially in the Livia vein. Galena shows high amounts of Ag, Bi, and Sb, while sphalerite registers the highest values for Mn and Cd (Costin, 2005).

Environmental impact on surface waters

The main effect of the negative impact of mining of the Văratec ore deposit on the environment is represented by the acid mine drainage. The acidic waters mainly originate from the surface pumping of the mine effluents resulted by underground oxidation of sulfides and sulphosalts, especially pyrite. These acidic waters are carried by a close channel from mine entrance to the ore processing plant where they are mixed with slurry and sent to tailings pond. Due to the bad maintenance, the channel is often clogged up and the acidic waters are released and mixed with surface waters. This process can be observed in Văratec Valley at approximately 500 m downstream of mine entrance.

The interaction of acidic waters with clean surface water has been studied in two points: the mixing of acidic waters with unaffected Văratec Valley (nr. 3) and the mixing of affected (in previous point) Văratec Valley with unaffected Izvorul Alb Valley (nr.5). In each point, three water samples were collected: two upstream of confluences (A, B) and one downstream (C). Three sets of analyses on water samples were made between October 2004 and April 2005. The parameters analysed in the field with a multimeter instrument (Consort 533) are: temperature, pH, Eh, conductivity and total dissolved solids (TDS).

The sample of mine waters evacuated from underground and collected at the entrance of the mine has the following parameters: pH = 2.97, Eh = 217 mV, conductivity = 4.00 mS, TDS = 2.17g/l. One sample of pure water from a spring was collected in order to evaluate the influence of mine waters on surface waters. The analyses indicate: pH = 8.24, Eh = -73 mV, conductivity = 413 μ S, TDS = 220 mg/l.

Downstream of Văratec Valley to mine waters confluence, the quality of water valley deteriorates: the pH value decrease and the value of TDS increase (Fig. 1 and Fig. 2). Between the point nr. 3 and nr. 5, the pH values increase and the TDS values decrease indicating a dilution process caused by the mixing of water from Văratec Valley with other

small creeks. Further dilution is taking place after the confluence of Văratec Valley to Izvorul Alb Valley, the second stream being an water course unaffected by mining activities. These variations can be observed very well for the analyses made on 22.10.2005 and 25.11.2005. On 07.04.2006, the flow rate of the surface waters was quite high due to the snow melting and rainwater, therefore the variations of pH and TDS are very small.

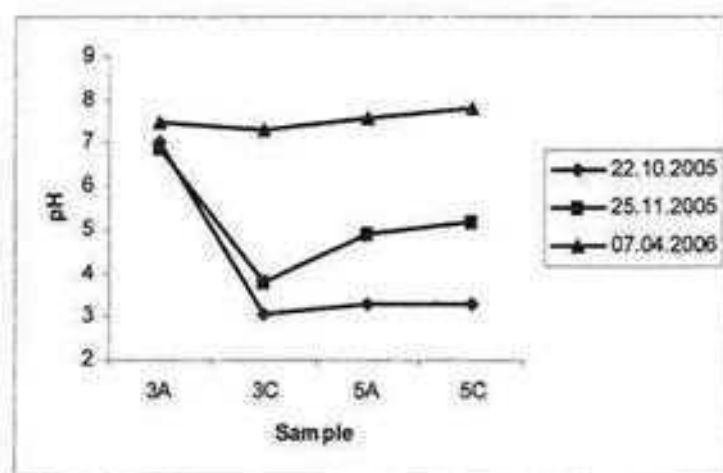


Fig. 1 – Variations of pH values downstream Văratec Valley

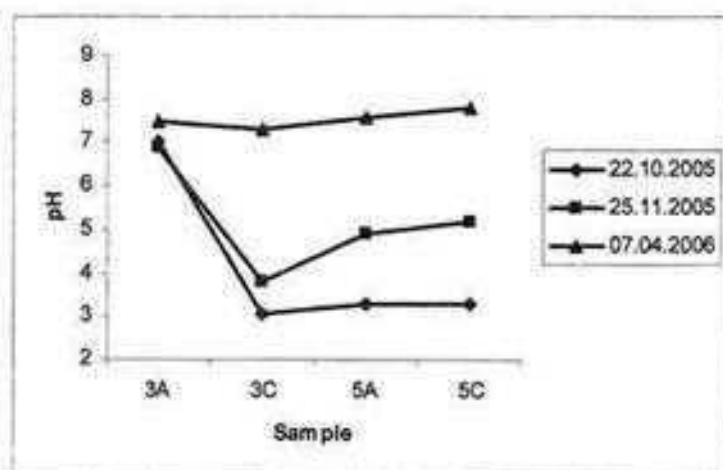


Fig. 2 – Variations of TDS values downstream Văratec Valley dissolved in water.

Further researches are necessary to evaluate the level of metal pollution in Văratec area. Previous studies concluded that the Băiut region is one of the most polluted zone form northwestern Romania (Bird et al, 2003). But these studies were made downstream of Băiut village (samples from Lăpuș River) without indicating the source of pollution. In the Băiut region there are located several pollution sources like: mine water form Văratec Mine and Breiner Mine, ore processing plant, pipe line which transports the slurry from plant to tailings

Conclusions

The main environmental issue related to mining activities form Văratec Mine is the negative impact of mine waters on surface waters. These mine waters having an acidic character result form oxidation of sulfides, the main constituent of the ore deposit. Due to the bad management, the mine waters mix with surface waters causing a deterioration of water quality.

Generally, downstream of confluence with mine waters, the water form Văratec Valley has small pH values (acidic waters) and high values of total dissolved solids (TDS). The high values of TDS indicate the presence of heavy metals (Pb, Zn, Cu, and possibly other metals like As, Bi, Sb, Cd) compounds

dam, one active tailings dam, one close tailing dam, one tailings dam used for deposition of pyrite concentrate. More detailed studies have to be made to determine the environmental impact of each source of pollution.

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SHORT HISTORY OF TURDA SALINE MINING

Rock salt systematic mining at Turda Saline begun in the period of Dacia occupation by the Romans. The mining was made by open pits and the excavation shape was similar with actual quarry geometry.

After the Aurelian retreat in the year 271, the historical proof concerning the rock salt mining is missing. Only since the year 1075 there exists a document released by the Hungarian Chancellery, which confirms the existence of a rock salt custom at Turda, on the Aries and Mures road and, indirectly, confirms the existence of rock salt mining activity.

MINING METHODS

The rock salt mining in bell shaped rooms performed until the end of the XIXth century at the Turda Saline is presented in Figure 1.

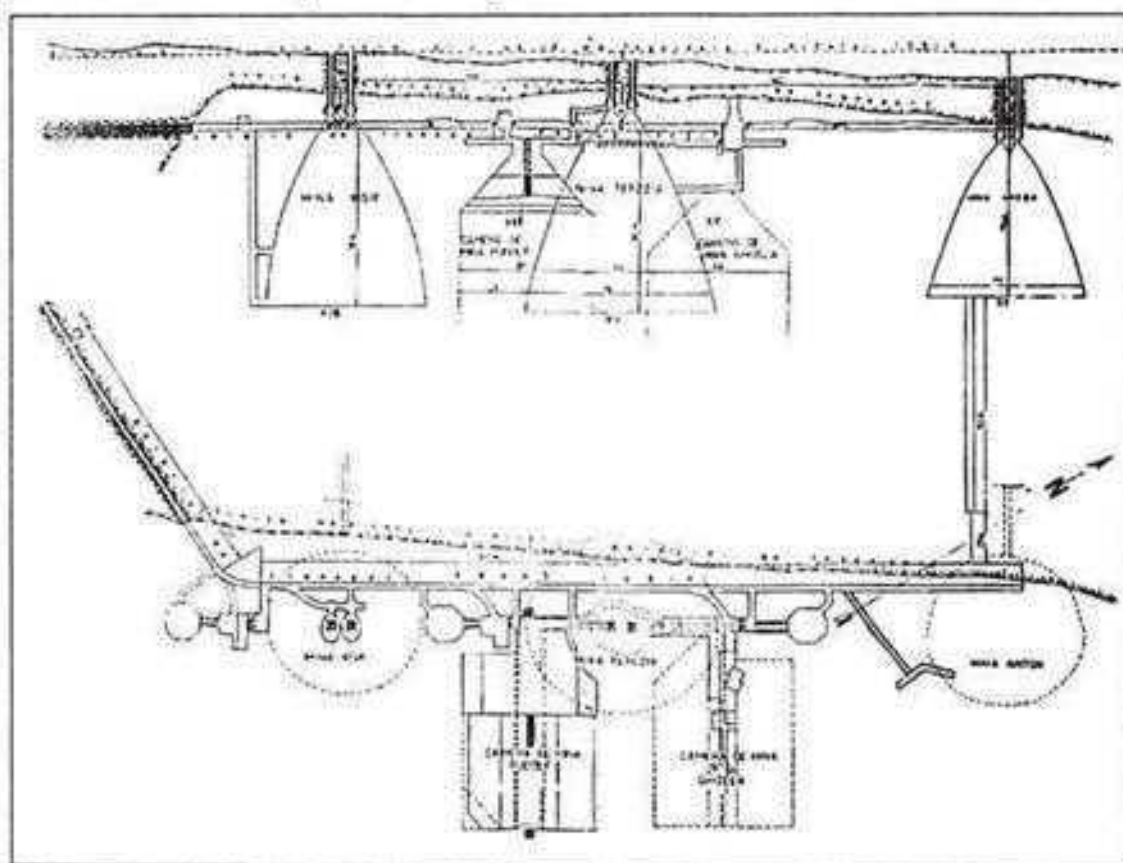


Figure 1.

The room opening was made through a pair of shafts with the digging section of approximately 7.8 m^2 . The distances between the shafts' axis was of 8 m. Oak beams in organ timbering made the shaft support. The used section after timbering was of 6.25 m^2 . In order to prevent the beam sloping, the oak beams were fixed in the hitches dug in the shaft wall at a distance of 5m, after the ferruginous sedimentary covering crossing, the shafts continued to be driven at the initial section in the salt, at a 8-10m depth. In this way the ceiling, which had to support the pressure of covering rocks, was made.

At approximately 5m from the rock salt entrance, the support units were embedded in the hitches 2m deep in the salt. The mining room opening begun at the shaft bases by conical excavation achievement, which was enlarging, joining into a single bell. At that moment, it could be said that the mining room opening was achieved. At the same time with the room driving, its diameter was increasing, reaching 60-70m to a final 100-110m depth.

When reaching these sizes, the mining rooms were abandoned, because of the difficulties of vertical transport of mined rock salt. The rock salt was evacuated at the surface with the aid of a hoist with vertical axis, acted with the horses' power, situated on the surface, in the common direction of the two shafts' axis.

One of the opening shafts was arranged for rock salt transport, and the other one, for the workers circulation, being equipped with rope ladders.

Because the bell shaped saline mines had a continuous danger of flooding and rock faulting, which lead to the premature abandoning of the salines, they were replaced with big trapezoidal rooms methods.

The trapezoidal rooms methods were experimented at Costui (Maramureş) in the second half of the XVIIIth century, which were also applied at Turda saline.

The trapezoidal rooms were opened at Turda saline through driving a vertical shaft from the underground. The preparatory galleries of a new type of room started from the shafts. From the axial preparatory gallery with a length of 85-110m was executed the enlargement of the rooms at the ceiling level until the 12m span, after that continuing with the rock salt mining at the floor level. The circulation compartments for the workers access were arranged at the longitudinal axis extremities of the room, on the face floor, equipped with ladders and resting stages. Balconies were built at a depth of 4-6m, which allows the access at the descending ladders in the room. Wedges made the beams' fixation in the hitches.

The room driving continued at the same span another 2m, afterwards began its enlargement. To maintain the room stability, the enlargement was made at a 45° inclination. When the room's width reaches 50m, the walls are returning at a vertical position. The maximum mining depth of the rooms was approximately 75m.

The rock salt mining was made through the delimitation of a rock salt block from the floor room with a 4m length and a 1m width by digging a contour kerf on a 30-35 cm depth.

The kerf's digging was made with hammers with a sharp end, having a weight of 2-2.5 kg, equipped with an elastic tail of 60-70 cm length; wedges were introduced in kerfs for the detachment of the floor blocks. The resulting block was cut in pieces weighing 12-15 kg. The rock salt pieces weighing 48-52 kg were named "formal rock salt" and were used as a financial currency.

The rock salt extraction by blasting system was experimented after the year 1868 in Turda saline; but because this procedure resulted in too many small rock pieces, it was abandoned. The rock salt was extracted in the Iosif, Terezia and Anton rooms until 1862 and in the Rudolf and Ghizela rooms after 1870, when the Franz Iosif adit was finished.

After the First World War, the rock salt mining becomes a state monopoly, and because of the competition between the Ocna Dej and Ocna Mureş salines starts the decline of the mining activity of Turda saline. The last face of Turda saline, the Rudolf room was closed in 1932, a year that marks the ceasing of rock salt mining after almost two millenniums of activity.

TURDA SALINE-MUSEUM-WATERING TREATMENT BASE

In the year 2000, Turda saline, together with Sărăturile Turzii and Ocna Veche Turda, was declared a natural reservation of national interest.

To allow tourists' access in the underground a checking of underground excavation stability was made and as a consequence of the studies results the following conclusions: Iosif, Terezia, Rudolf and Ghizela rooms are stables, also the pillar between the Rudolf and Ghizela rooms; the ceiling rooms present a good stability.

Taking into account of rooms stability on the following period we make the following propositions: detailed study of rock salt geomechanical characteristics of Turda Saline, including the rheological characterization; monitoring, with a adequate apparatus, of fissures development in the walls and ceiling and the scaling of rooms; study of room stability in interaction by numerical modelling, taking into account of intersection between Rudolf and Terezia rooms.

In view to ensure the access into underground of Turda Saline the following workings are necessary: floor rectification-concreting of Franz Iosif gallery; floor skimming of access workings in the Iosif, Terezia, Rudolf and Ghizela mines; walls and ceilings smoothing of Gizela mine; floor rectification of Iosif, Rudolf and Ghizela rooms; isolation dams

construction of Anton mine; arrangement of the exit on the incline working from the Sărată-Durgău Valley; driving of staple for sanitary groups emplacement in the Rudolf room.

The minimum cost of these arrangements are estimated at 626 138 RON.

In order to ensure patients' comfort, the rooms have to be equipped with furniture, panoramic elevator for the access into Rudolf room and other facilities (lighting, sport fields, ventilation, etc.) which are estimated at 800 000 RON.

Respiratory system diseases are at the pick of morbidity as frequency and severity index. Between the therapeutic methods that use the climatic factor in the respiratory system treatment, a specific aspect is represented by saline microclimate.

The first researcher that noticed the beneficial effects of a long exposure in the saline atmosphere of the patients with lung diseases was the polish F. Boczkoisk. The favourable results were attributed to some specific conditions, observed in these treatment places: the constant air temperature (11-12°C); the relative humidity with small variations for the same saline, but with large variations in different salines (73-83%); air movement is practically neglectable (0.1-0.3m/s); salt aerosol presence in the form of solid particles; small aeroions in variable quantities with the predominance of positive ions (nt 251-584; n-224-461 the report $q(n^+/n=1.12-1.75)$); the allergens' concentration is practically zero in all the ventilated salines; the lack of aeropollutions and pathogen agents.

CONCLUSIONS

Turda saline's underground can be arranged for visitors' access with minimum costs.

The saline has large spaces, isolated chambers without air currents, the mining activity is stopped, therefore optimal conditions for therapeutic using are existing.

The microclimate measures in the saline are a guarantee that the saline can be used with good results in a therapeutic purpose.

A GUIDE OF ENVIRONMENTAL MANAGEMENT SYSTEM IMPLEMENTATION IN MINING ORGANIZATIONS

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During environmental management system (EMS) implementation, the mining organization's manager suffers a lot of pressure and he may be oneself responsible for all the problematical situations. To keep away from such circumstances, managers had to know when they must to decide or involve subordinates in decision-taking process and when they have to stand and wait a certain opportunity. In EMS implementation process, managers of mining economic organizations assign themselves objectives according the environmental standards, accommodating those with the organizations general objectives. It proceeded with environmental targets assigning, translated in proper actions that consisted in systematic solving of problems suggested by the impact of mining activities with over natural environment.

In an obvious logic, some factors linked with the objectives assigning process can impose organizationally limits to decision, so as:

- fondness scarcity to proposed environmental objectives;
- collision between general management objectives and environmental objectives;
- the given values of one or other mining economic organization;
- cultural limits.

To simplify, managers, when they decide the EMS implementation, there are in classic situation of "3 by 3", namely: tree types of decisional problems, tree decisional situations and tree possible ways to approach decisional situations (Figure no. 1). This is the moment to use any instrument that brings help. Implementation of the EMS means a process that superimposing over the general management system tasks a new system of management, as ISO 14000 standards family required.

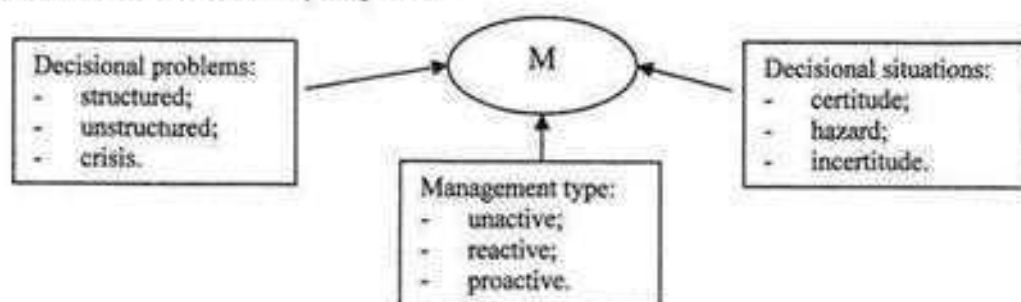


Fig. no. 1 The "3 by 3" situation in management decisions

In Figure no. 2, tree levels are introduced, populated as it follows:

- On the strategic level we find the decision team, which include obviously the top-manager.
- On the tactic level we find the chiefs of functional structures, who can be assimilated with the chiefs of mines and careers, together with decision teams.
- On the implementation level we find medium technical personnel (the level of a foreman), who can take confined decisions, linked with current tasks.

The key of the whole process is efficacious communication; inside the organization and out with the surroundings (interested parts). Efficacious communication vehicle is the informational system, which can be compared with a neuronal network of a living organism.

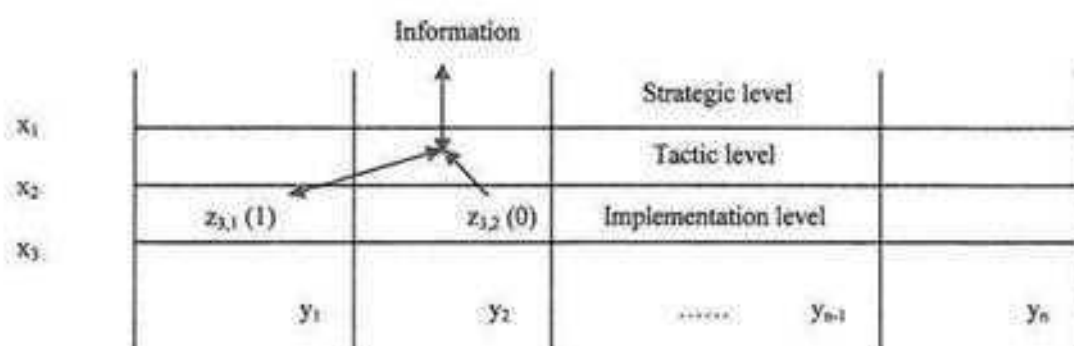


Fig. no. 2. Decomposing organizational system and its conformity with individual "address" of employer

Thus, every employer will be located as a target for discreet information by some coordinates, respectively: $A(x,y,z)$, where: x - functional level, y - domain, z - addressee qualification. In this tree dimensions space, environmental information can follow two ways: down and up. Communication of environmental policy between levels is possible after decomposing, in accordance with the manager decisions. The running space, crossed over down and up by an information wave.

Characterizing thus the employer's position, the next step is the introduction on the program of that information which will "teach" informational system to supply every employer with necessary environmental information. Environmental information of a common nature must be accessed permanently, irrespective of the x , y and z . This is environmental information that has to be known by all employers; such is the case of commitment list regarding environmental policy of organization. The access of granted addressee to environmental general information can be accorded, with general manager's decision, to interested parts: mass media, NGO's, circumstantial co-workers.

Environmental information of a specific nature mostly designates a family of specific environmental information of level '0', '1' or '2'. Environmental information of level '0' is destined to feed decision team: top manager, environmental chief, environmental counselor, technical directors, chief-engineers, involved in couching of environmental policy decision, depending on professional tasks registered in employers job record. Addresses for access to level '0' environmental information can be earmarked, according to the general manager's decision, also for external addresses; auditors, environmental authority. Level '0' information is defined as environmental information that allows strategic decision.

Environmental information of level '1' is destined to the tactic level: mine chiefs, career chiefs, mine/career chief-engineers, sector/department chiefs, depending on the access level imposed by the general manager. For those who populate this level and access to environmental information are restricted, $z = 0$. Specific information of level '1' is differentiated also according to the value of 'y', so that $A(x_i, y_1, 1)$ beneficiaries by a different information than $A(x_i, y_2, 1)$.

Environmental information of level '2' is destined for implementation level. It includes mostly demands and instructions. The access level granted by employers on this level allows to every $A(x, y, z)$ to introduce in the system that environmental information which setting up feedback wave. For feedback route procedure is that: the environmental chief – or other employers with environmental responsibilities – will set up periodically (at the interval ordered by the top manager), or in certain established situations, reports which contains the environmental information, necessary in adequate foundation of environmental policy decision. To facilitate the communication of those reports, following demands are requested:

- Reports will contain only that information which can complete the pre-existent information. To facilitate the interaction with the informatics system, reports will be standardized, so that what is written on paper must be found in the informational system's database. We recommend the model open in Figure no. 3.

Imperative: Yes No	
ENVIRONMENTAL REPORT	
Addressee position: x y z	
Data: day month year	
Problems referring to (text):	
Worked out by: (last, then first name and x y z	
Measures taken (text):	
Level of directly measures: x y z	
Addressee motion (text):	
Execution data:	Executed by: x y z

Figure no. 3 Environmental report model

- Reports will be kept in the system's memory and paper support will be stored in archives or destroyed.
- Environmental reports will have a supplementary mention regarding the urgency degree.

A "Guide" of EMS implementation in a mining economic organization from Romania was conceived as a software program of database. It was built up by algorithmizing the steps according to ISO EN SR 14001 and 14004 standards demands and then by adjusting them to specific nature of economic organizations working in Romania's mining industry. Three ideas enliven us from the beginning: to help the Romanian mining organizations general management to understand ISO 14001 and 14004 requirements (generally, ISO 14000 standards family); to help mining organizations for bettering informational policy, as an EMS implementation necessary premise; to support EMS implementation with an aggregate informatics product, an implementation guide, conceived so that respects ISO 14001 and 14004 standards requirements and the requirements of a modern communication policy.

The main adding value is the "incorporate looking", a design method which allowed to built a versatile and easy-using instrument as the EMS Implementation Guide (Database ECO_2004) there are.

Further data can be obtained in the following papers and books:

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- Felea, C. M., Georgescu, M., Matei, R.** (2004) Considerations regarding the role of informational system to assist environmental policy decisions in the mining organization. Thirteenth International Symposium on Mine Planning & Equipment Selection, Wroclaw, Poland.

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THE CHEMISTRY OF M'DHILLA PHOSPHOGYPSUM OF TUNIS

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Introduction

Phosphogypsum is the by-product of the phosphoric acid industry and is obtained by reacting phosphate rock with sulphuric acid. Approximately 7 million t of this by-product has already been produced by the phosphate Tunisian Chemical Group, with a production of 11-million t / year. Although phosphogypsum is mainly gypsum, it contains quartz and elevated levels of impurities, which originate primarily from the phosphate rock used as raw material. All of this material is stockpiled because the impurities prevent its utilization.

This study aims at characterizing phosphogypsum for a possible the commercial use may be of the production of cement instead gypsum, as a soil amendment and as in the paper industry substituting limestone.

Phosphate acid Process

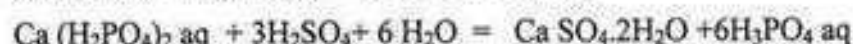
The Tunisian Chemical Group uses the process Di hydrate called SIAPE. The phosphate rock is reacted with sulphuric acid (98% content) and the temperature is ranging about 78 to 80°C. This process results in the production of phosphoric acid (28% content) and of substantial quantities of gypsum by-products, known as phosphogypsum, according to the reaction:



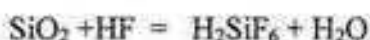
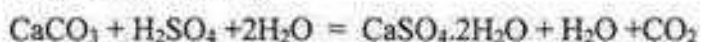
$n = \frac{1}{2}$ Hemi-hydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$);

$n = 2$ Di hydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

This reaction is done in two simultaneous stages:



According to the presence of the impurities in the phosphates rocks, there will be other secondary reactions:



The M'Dhilla region is characterized by very salted water rich in NaCl. It is an important factor, this water is used all along the process of production and will have an important role on the crystallization of the various phases during chemical reactions. The water of washing not recycled and the fines particles are rejected into the river.

The Phosphogypsum, the by-product of the phosphoric acid industry, is stockpiled in Talbia of M'Dhilla. All the phosphogypsum samples studied were, therefore, prepared by drying at a temperature not greater than 45°C to constant mass, ground to a grain size of less than 250 µm and finally stored in a desiccators' at room temperature.

Analytical procedures

The analytical methods used in investigation were scanning electron microscopy (SEM), inductively-coupled plasma - atomic emission spectrometry (ICP-AES), X-ray fluorescence (XRF), Fourier-transform infrared spectrometry (FTIR) and X-ray powder diffraction (XRD).

Major and trace element concentrations were determined by inductively coupled plasma - atomic emission spectrometry (ICP-AES), excepting sulfur, which was determined by ion chromatography.

Powder dispersed on double-sided sticky tape and gold coated was also checked for chemical composition on a JEOL JSM 840 scanning-electron microscope (SEM-EDS) fitted with a TRACOR Northern 2000 energy-dispersive system. The apparatus was set at 15 keV, 5 nA beam current and a 10 µm raster were used. The standards used for calibration were fluorapatite (Ca, P), anhydrite (Ca, S), synthetic oxides (Mn, Fe, Mg) and chlorides (Na, K) and data were reduced with ZAF software. In all cases, due to the small size of crystals and of their instability under the electron beam, the results obtained were of poor quality; only

qualitative details were retained, consequently. The same apparatus was used for acquiring SEM images.

X-ray powder diffraction (XRD) analysis was performed on a Siemens D-5000 Kristalloflex automated diffractometer equipped with a graphite-diffracted beam monochromator (Cu K α radiation, $\lambda = 1.54056 \text{ \AA}$).

Textural and morphology relationships

Gypsum is the most abundant mineral of the assemblage examined. SEM observation shows that the gypsums are mainly formed by needles and rhombic types, rarely by globular aggregates. The gypsum is crystal up to $10 \mu\text{m}$ thin and $40 \mu\text{m}$ wide.

Ardealite occurs as earthy white aggregates, deposited on crusts or as efflorescence's in border of gypsum. SEM images show that the mineral generally occurs as aggregates composed of very thin, randomly disposed. The individual crystals do not exceed $10 \mu\text{m}$ in length, and are up to $2 \mu\text{m}$ thick and $10 \mu\text{m}$ wide (*fig. 1*).

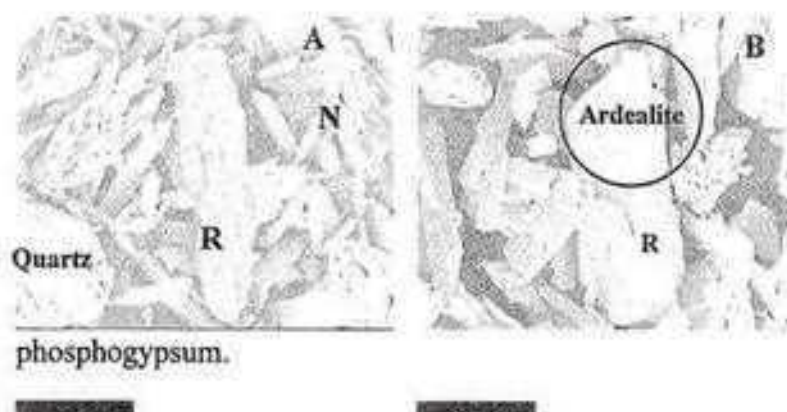


Fig. 1. SEM photomicrographs of phosphogypsum. A: Needles type and Rhombic gypsum and quartz; B: Little crystals of Ardealite on the rhombic

Chemical data

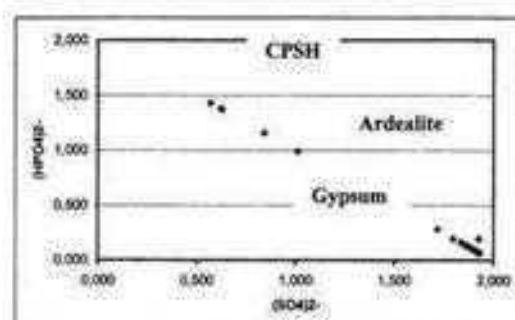
Energy dispersive spectroscopy (EDS) quantitative analyses of all the described morphologies show different compositions in different part of the same phosphogypsum sample. Note that the relative amount of SO_4^{2-} and P_2O_5 changes in the different points, but when P_2O_5 decreases, SO_4^{2-} always increases. Since the relative proportion P_2O_5 in the different part of phosphogypsum crystal. The efflorescence aggregates or small crystals on phosphogypsum show the high $\text{P}_2\text{O}_5\%$ content almost equal to those of SO_4^{2-} .

The detailed analysis show tow populations the Ardealite type with $\text{SO}_4^{2-}/\text{HPO}_4^{2-}$ ratio near to 1 and the CPSH calcium sulphate phosphate hydrate with $\text{SO}_4^{2-}/\text{HPO}_4^{2-}$ ratio between 0.4 - 0.5, whose chemical formula corresponds to $\text{Ca}(\text{HPO}_4)_x (\text{SO}_4)_{1-x} \cdot 2\text{H}_2\text{O}$. This phase nucleates and grows on borders of rhombic phosphogypsum and same times it is aggregate or efflorescence. The all crystals phosphogypsum, Ardealite and CPSH are characterized by high

Na₂O contents (0.18 up to 7.80%) due of the water used for the production and the washing. Na replaces the Ca in crystal.

Table 1. EDS analyses of selected samples of phosphogypsum (1-5), Ardealite (6-7) and CPSH (8-10).

	1	2	3	4	5	6	7	8	9	10
Na ₂ O	0,80	1,93	0,80	0,53	0,80	7,80	1,87	7,30	0,00	0,00
CaO	31,28	30,90	31,28	31,71	31,28	19,87	29,54	20,69	32,58	32,58
SO ₃	42,48	43,53	43,82	43,65	43,53	17,38	20,85	12,98	11,72	12,81
P ₂ O ₅	3,11	1,92	1,59	1,79	1,92	26,90	22,99	31,85	33,28	32,06
H ₂ O	22,34	22,62	22,51	22,32	22,47	24,08	21,95	27,17	22,42	22,56
Total	100,00	100,00	100,00	100,00	100,00	96,03	97,19	100,00	100,00	100,00
Na	0,080	0,103	0,080	0,053	0,080	0,780	0,187	0,730	0,000	0,000
Ca	1,920	1,897	1,920	1,947	1,920	1,220	1,813	1,270	2,000	2,000
(SO ₄) ²⁻	1,866	1,917	1,932	1,923	1,917	0,843	1,011	0,630	0,569	0,621
(HPO ₄) ²⁻	0,134	0,083	0,068	0,077	0,083	1,157	0,989	1,370	1,431	1,379
H ₂ O	4,000	4,000	4,000	4,000	4,000	3,693	3,783	4,000	4,000	4,000



Conclusion

Ardealite and CPSH crystallized tardily in very acid context by direct precipitation of the solutions saturated with ions sulphate and phosphates in open system of solutions

supersaturated in ions.

The injection of the recycling water of slurry washing very acid rich in P₂O₅, changes the relationship between H₂SO₄ and HPO₄²⁻ in the reactor. This modification of H₂SO₄/HPO₄²⁻ ratio produced a small Ardealite and CPSH crystals.

RINAUDO, C. & ABBONA, F. (1988) and ASLANIAN, S. & STOILOVA, D. (1982) were obtained in an acid pH the synthetic Ardealite and CPSH. First formed nuclei have a certain content of H₂SO₄ and HPO₄. Their subsequent growth involves the continuous incorporation of Ca²⁺, HPO₄²⁻ and SO₄²⁻ in the structure. When growth stops, it may happen that solution still supersaturate with respect to gypsum.

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GEOCHEMICAL STUDY OF WATER SAMPLES IN THE UPPER COURSE OF THE SÃO FRANCISCO RIVER NEAR TRÊS MARIAS, MINAS GERAIS, BRAZIL

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Introduction:

Minas Gerais is one of the most important mining regions of Brazil, only ultra passed by the Amazonian activities. Therefore the rivers, which cut Minas Gerais, are strongly subjected to pollution of heavy elements liberated by these specific activities.

The principal subjects of this study are the mining and refining activities of Zn in the industrial plant of CMM in Três Marias at the border of the São Francisco River. The ore come from two mines in Bambuí Group rocks. The Vazante Mine is with silicate Zn ore and the Morro Agudo Mine is with Zn-Sulfite ore. These mines are 200-250 km distant from Três Marias in western direction. The material is transported by trucks at the BR-040 as H₂SO₄, too.

This paper compares investigation done in 1986 with investigation in 2002 to evaluate the actual ambient situation in the part of the São Francisco River between the Três Marias Lake and river down of the Zn Production Plant of the CMM (Companhia Mineira de Metais), part of the Vontorantim Group. We tried to show the development of pH and the concentration of selected elements in the São Francisco River between the Lake and the Zn plant near Três Marias from 190 till 2002.

Zn refining process:

In a triangle between the river, the city and the road from Brasília to Belo Horizonte the plant of Zn production is installed at the margin of the river. The old basin of deposition was installed close to the river and in rainy period waste products entered the São Francisco. The decontamination basin nowadays is transferred to a region along the river, but the metals still in this part may have an influence to the river.

After the transport of all raw materials by truck to the Três Marias plant, the processing begins with drying and grinding. During the proceedings a lot of dust, smoke and vapors are liberated and need to be captured. Acid cleaning and process water are transported to the decontamination basins before liberating to the São Francisco River. There occur a mixture of water of different origin with variant pH and composition. This water is cleared and prepared to conditions close to tat of the river.

The processes used by CMM to refine the material that come from Vazante e Morro Agudo Mines are visible. After separate processes of enrichment and with the production of H_2SO_4 ($SO_2/O_2/H_2O$) by treating the Sulfite-ore processes of flotation and decantation separates the Zn-ore from sterile, which is deposited in the basin, containing still some percent of metals and pH above 9.

Older works:

The Commission of Environmental Politics -COPAM (1986, 2003) is monitoring since a long time, the volumetric variation conditions of the San Francisco River and his tributaries, and also, the quality of the water at selected places. They observe, mainly, visual parameters and the biological quality. This produces basic data for the evaluation of the steady state of water upstream from the Zn plant and COPASA (de Souza, 1993)

Other investigations were made by CETEC (1985), which lead to the obtaining of chemical data of the water in the contributors and the Três Marias Lake.

The most recent works, outside from CMM data and FEAM, date from the period from 1990 to 1992, when works of Master's degree were accomplished. This work show that the São Francisco River come relatively clean out from the Lake were the contaminant from contributors are deluded till under the norm data from CONAM (1986).

Some basic data from of Três Marias Lake:

1. The tributaries of the Três Marias Lake show pollution types that varies with the activities installed at the margins:

- a. Paraopeba River: Metallurgical industries of Sete Lagoas and pollutant that come from city of Belo Horizonte (pH: 4.4-4.8; In the: 6-8ppm; Mn: 0.2ppm; Al: 1ppm; dark; high turbidly).
- b. Indaiá, Borrachudos, Marmalade and upper San Francisco River: typical pollution of agricultural areas and sugar mills (pH: 4.3-5.8; In: 0-2ppm; K: 0-1.3ppm; Mn: 0-0.1ppm; Al: 0-1.3ppm. In one sample occurred precipitation of S-compounds?

2. Profiles over the lake show a dilution of the primary pollution of the tributaries (pH: 5.45-5.5) towards the dam (pH: 5.5-5.55; In the: 2-3ppm; K: >1ppm; Al: 0-1ppm) and a certain contamination for the traffic of rafts and boats (pH: 5.5-5.6; Al: 24-25ppm).

3. At the downside of the dam and still upstream of the bridge of BR-040 over the San Francisco River, happens a urban pollution originated for an village of the city of Three Marias and fish and pig creating farms (pH: 5.8; In the: 3ppm; K: 1ppm; Ass: 0.02ppm; Mn: 0.1ppm; Al: 0.5ppm Zn: 0.03ppm).

Passing through the lake the water suffers homogenizations that lead to a composition of water not far from normal concentrations without relevant pollution of heavy metals.

Results:

In the tables shown below is possible to see the concentrations of the determined trace elements and of the pH in relation to the localization on the river.

1990: The water upstream of Três Marias may be classified like class 5 of CONAMA and improper for domestic use. Some of the contributors (Paraobeba River) approximate the composition of waste water effluent (Lunghamer, 1991; Horn & Sgarbi, 1993).

All trace elements investigated showed an increase with the approximation to the Zn plant, especially in the surrounding of water caption (P1; near bridge Br-040) and the wastewater influx (P2; near Conciência River). High values were also found also at the margin close to the dam of the old retention basin. Mn and Fe are about permitted levels. The elements Zn, Cd, Pb and Cu are clearly correlated with the activities of the CMM plant. The pH is relatively low at the whole part of the river in front of the plant (Lunghamer et al., 1992, 1993).

2002: The water liberated in 2002 from the Três Marias Lake show and better composition like in 1990 with less contaminants without excessive concentrations of detected elements.

The pH moves on a normal scale. Pb and Ni were not detected. Mn and Fe values were generally lower. High Zn and Cd values occurred only in parts where the water is in contact with an inherited contamination of sediments.

Till 1990 the pH changes from limits around <5,5 to values near and above 6,5 excepting the part of the river in contact with the dam of the older decantation basin.

In 1990 all water of the São Francisco River after passing near the plant showed high values in Zn, beginning upstream from the bridge of the BR-040 until samples taken near the island in the river downstream of the plant. Extremely high values were found near the dam and in the Conciência River where the wastewater were introduced in the São Francisco.

In 1990 all the margins near the CMM plant were contaminated by high Cd values from the bridge of the BR-040 (pump 1) until the island. In 2002 the high-contaminated water samples were restricted of the former wastewater return of the Conciência River and the margins downwards. Probably these high values are due to the contact between the river water and still contaminated sediments.

Conclusions:

A comparison of the data obtained in the 90^{ties} with the data from 2002 show a significant reduction of heavy metals, pH and conductivity in the water near the CMM Zn plant.

Water from the Paraobeba and Velhas Rivers continue to be nearly unaltered.

The heavy activities of the governmental organization to preserve the ambient conditions and to pressure the industry, communities and agriculture to reduce the input have been fruitful. There is still work to do to change the condition of still affected parts of the São Francisco River.

Acknowledgement:

We acknowledge to the CMM and the laboratorial stuff for help by sampling and for intense discussions. CNPq, FAPEMIG gave financial support. CPRM and CPOMTC-IGC gave analytical support for this work.

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FLUID EVOLUTION AND GOLD GENESIS ALONG A SHEAR ZONE IN THE NORTHERN LEAOTA MOUNTAINS

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The Leaota Mountains can be seen as a set of homogeneous petrographic bodies (lithons). The mono-axial lithons are parallel and they form a lithonic arrangement, which is basically horizontal. The mono-axial lithons are generally oriented in the NW-SE. The longer axis direction of the mono-axial lithons is the same as the direction of the mineral lineation of the rocks that form the lithon. The mineral lineation of the tabular lithons rocks is the same as the mono-axial lithons lineation.

The horizontal direction of the lithonic ensemble and of the lineation suggests the fact that the movement had an important horizontal component.

Most rocks from the Leaota Mountains have a clear anisotropy, which is given by the preferential orientation of the minerals, but also by their preferential location. Very strong L-S fabrics have developed there, and in some cases with an extreme decrease of the granulation and a typical presence of porphyroclasts.

The rocks generally represent a lineation that is defined by the minerals elongation and, sometimes it has a ribbon-like character. Once it is formed, the foliation represents heterogeneity and may become penetrable, having a progressive deformation.

In general, the lineations have small inclinations, as well as the schistosity planes. Where we can see a deviation from the horizontal position, we are able to macroscopically observe the presence of some fractures, which made the schistosity planes become almost vertical. As we move away from the fractures we can see that the planes become almost horizontal again.

On every outcrop, we can often recognize the presence of two mineral lineations that are overlapped on the same carrying surface: one is orientated NW-SE and one is orientated NE-SW. The NW-SE one is mainly given by the biotite orientation. The NE-SW lineation is usually given by the chlorite. This last ductile deformation (that had as a result the NE-SW lineation), led to the rocks retromorphism, the most frequent being the passing of the biotite in the chlorite.

In spite of all these, the tectonic architecture from that area is given by the NW-SE deformation.

The mineral lineation is the consequence of the sin-kinematic reorientation. The lineation indicates the relative movement direction.

The crystals that mark the schistosity planes have developed through sin-kinematic crystallization. The schistosity planes acted like some gliding planes.

In the Leaota Mountains, the anisotropic fabric of the rocks is a consequence of the deformation. The main deformation mechanism was the general shearing, planar strain regime. The kinematics indicators show an eastern movement for the deformation oriented in the SE-NW and a movement towards SE-NW for the deformation oriented in the NE-SW.

From a petrogenetic point of view, almost all the petrographic types are tectonites, with the deformed fabric developed under the conditions of a mylonite or a cataclastic running.

Most of the rocks that have been studied are either mylonites or blastomylonites. They were able to form themselves out of rocks that initially were isotropic (granite) in the conditions of a ductile deformation.

The microstructure study points out the fact that the Leaota Mountains has a very complex deformation history, having at least two moments of strong deformation under ductile conditions, which led to forming the shearing areas: a shearing area oriented NW-SE, and a later one oriented NE-SW. There can also be seen very strong interactions between the rocks and the fluids, which suggests that these late deformations have encouraged a strong fluid running, which in the end led to the alteration and sometimes to the mineralization of the affected rocks.

In the field, there could have been seen two main systems of fractures: a NE-SW system (older) and a NW-SE (newer).

Except fractures, there have been observed the gliding scratches, too. In both fractures, the gliding scratches are, usually, horizontal and parallel to the mineral lineation of the rocks surrounding the fracture. The horizontal position of the gliding scratches proves that the movement had a horizontal ruling component, with strike-slip fractures.

The two main systems of fractures can also be found in the Jurassic limestone from the Leaota Mountains. This proves that these fractures have been active from a tectonic point of view even during the alpine orogenesis.

The gold can be found in native state in quartz. The structural observations show that the auriferous mineralization was formed in a shearing area developed in the NE-SW direction. The auriferous bodies can be found in the brittle – ductile structures.

The mineralization appears as small shear lens and can be found in the NE-SW fractures, which are parallel to the penetrating schistosity planes from the rock.

The mineralization was formed during the same deforming event that generated the shearing area, probably at the brittle-ductile limit of this area.

The deposition processes, both metasomatic and void filling, had a sin-kinematic character. They were controlled by: deformation, structural-tectonic setting and petrography.

The deformation represents the main controlling factor. It shaped the morphology of the ore-bearing bodies, and the Au concentration.

The structural-tectonic setting represents a shear zone.

The petrography was important, as the rocks with high Fe contents are more able to host Au ores, where the Au transport was done through chlorides.

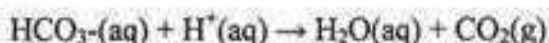
The late movements on NE-SW and NW-SE fractures, which also affect the sedimentary rocks (Jurassic limestone), spatially reorganized this mineralisation.

The petrography and the fluid inclusion microthermometry showed that the Au-bearing quartz precipitated from a homogeneous fluid made up of H₂O, CO₂ and salts. The microthermometric data showed that NaCl and KCl were the main dissolved salts.

The metal transport in the shear zone was made through chlorine-based complexes.

This conclusion is based on the following data:

- the concentrations are rich in quartz and poor in sulphides, showing a low pH for the fluids (the same is shown by clay alterations)
- the fluid-rock interaction (hydroxides on pyrite) showed that the fluid had a high Eh
- available Cl⁻
- for the Cl⁻ based compounds:
 - lowering pH and raising Eh dissolves Au
 - raising pH and lowering Eh concentrates Au
- the separation of the CO₂ fluid from the H₂O-rich one in the fluid inclusions with an immiscible watery content raises the fluid pH (Reed, in Spycher, 1985), because of the reaction:



The interaction between fluid and an oxidant environment leads to the reduction of the solutions (the oxygen activity decreases) and the gold precipitation from chlorine-based complexes.

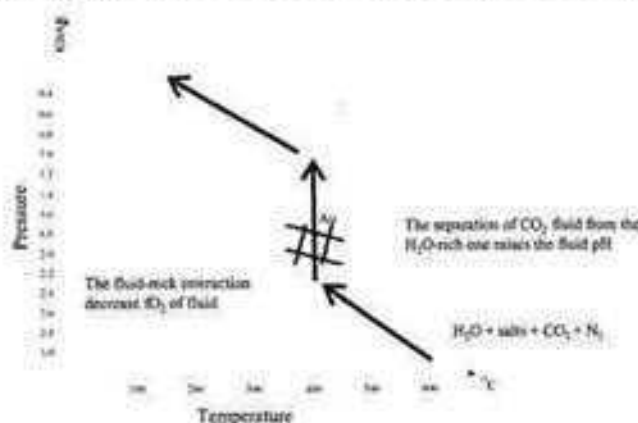
In the gold-bearing quartz one observes the coexistence between miscible, pure CO₂ and H₂O + salts fluid inclusions. The syn-genetic characteristics of the inclusions from the same sample may suggest immiscibility (Ramboz et al., 1982).

Assuming that the aqueous and the carbonic inclusions chosen for this determination resulted from separation from mixed inclusions, then using the method of the isochors intersection one obtains capturing temperature and pressure conditions for these fluid inclusions of about $T=420-150\text{ }^{\circ}\text{C}$ and $P=1.8-0.8\text{ kbar}$,

The shear zone localized the ascendant movement of the fluids through the crust. The fluid evolved during the ascension along the shear zone from the higher to lower pressure and temperature conditions. This fluid reacted with the host rock leading to its mineralization and alteration.

The parental fluid is interpreted as a mixture of $\text{H}_2\text{O}+\text{CO}_2+\text{NaCl}$ (about 10% NaCl-equivalent, dominated by NaCl-KCl). The temperature estimation for this fluid is about 450°C .

This high temperature, high oxygen fugacity and low pH fluids transported gold as chlorine-based complexes. The pressure drop around the brittle-ductile limit resulted in the separation of a CO_2 -rich phase from the H_2O -rich phase, thus raising the pH of the fluid. The pH of the fluid raises buffered by the pyrite-rich rocks and the fugacity decreases. The chlorine-based compounds are dependent on both fluid pH and oxygen fugacity. Consequently, the combined effect of the phase separation and the fluid-rock interaction leads to the metal precipitation at the contact between the pyrite and the oxidation zone.



Genetic model for gold mineralisation from northern Leaota Mountains

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THE QUALITY OF THE SURFACE WATERS FROM THE HYDROLOGIC BASIN OF AMPOI RIVER

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One of the primary components of the environment, intensively affected by the pollution from the hydrologic basin of Ampoi River, in Metaliferi Mountains, is the hydrosphere along with all its components i.e. surface, ground and meteoric waters.

In analysing of the waters from this area, one should begin with the system subcomponent that induces “the uncontrolled entries” from the factory for ore processing which, in different phases of the technologic process, discharges an estimable quantity of used waters. A bilateral relation is established between this phenomenon and the quality of the other components of the environment i.e. the impurities contained by the used waters which operates in most cases, in a negative way on the other components, but on the other way, especially the biotic component has an important contribution to the removal of some pollutants from the used waters, through the action of those microorganisms (bacteria) of biodegradable role. The researches undertaken on this subject demonstrated that, to a certain point, the surface waters own a special auto purification capacity, but in the case of some pollutant agents or when the specific “threshold” is exceeded, the auto purification does not take place because the microorganisms don’t have any longer the capacity required to produce a regeneration, so that, in these situations, the waters remain permanently septic (Fig. nr. 1).

A brief list of the potential dangers represented by the discharges of used waters from the factory in Zlatna, comprises:

- the contamination of drinkable water sources, as a result of the used water infiltration through soil in the formations that accommodate the surface water table;
- the direct impact over the health status of the population from that zone, by means of the effects produced by the substances of advanced toxicity;
- the degradation of flora and fauna from the surface waters and creation of conditions for developing of some parasite microorganisms (germs, bacteria, pathogen germs etc.);
- the introduction into the natural environment of some steady chemical compounds of toxic effect on long term, some of these compounds having the property of accumulating itself into the living organisms or to concentrate lengthwise of some trophic chains.

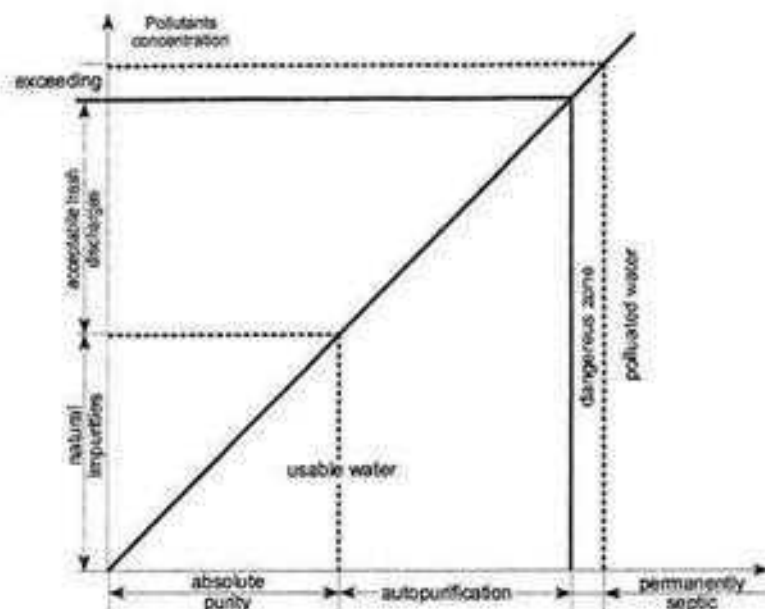


Fig. 1. Limits of eputation capacity

Each one of the units of the factory “contributes” to the discharges of used waters into Ampoi River. Thus, SC “Ampellum” discharges, in average, a quantity of 45 m³/hour used waters into Ampoi River; the proportion between the quantity of used waters and the natural debit of the river is approximately 1/1 meaning that at the exit from Zlatna, the river debit is doubling when receiving these waters with high level content of suspension material and heavy metals. The quantity of used waters comes mainly from the old factory (75%) while the “contribution” of the new factory is registered around 25 %.

A briefing of the chemical characteristics of the discharged waters underlines first of all their high acid character as well as frequent exceeding of the maximum concentration admitted for copper, lead, zinc, cadmium and iron, phenomenon observed at about 66%-85% of the analysed samples. This situation is the result, mostly, of the deficiently way of treating used waters before being discharged in the river.

The quality of the waters evacuated in to the Ampoi River was systematically monitored both for the waters derived from the new factory and for those ones from the old factory that doesn't own a purification station as it was stated before. The chemical characteristics of the evacuated waters from the two factories were systematically determined and the results for the period 1996-1999 are displayed in the table nr. 1.

Table 1.

Site	Indicator	CMA (mg/l)	Max. concentration (mg/l)				Medium concentration (mg/l)			
			1997	1998	1999	2000	1997	1998	1999	2000
New factory	pH	6.5-8.5	10	8,7	7,5	10	5,55	6,05	6,37	6,75
	Cu	0,05	88	63,7	2,31	5,14	20,37	4,09	0,35	0,46
	Pb	0,05	2,64	2,7	0,03	0,03	0,51	0,17	0,05	0
	Zn	0,03	1,8	1,08	0,5	1,64	0,71	0,16	0,19	0,32
	Cd	0,003	0,03	0,1	0,01	0,01	0,01	0,01	0,01	0
	Fe	1	1,6	21	10,6	10,1	0,47	2,3	2,53	0,99
Old factory	pH	6.5-8.5	7	7	7	10	3,86	5,43	6,25	6,33
	Cu	0,05	41,4	18,8	17,1	60,2	17,84	5,69	2,97	6,57
	Pb	0,05	1,69	2,02	0,1	1,34	0,46	0,14	0,02	0,13
	Zn	0,03	5,06	4,7	2,72	26,2	1,146	0,89	1,09	2,99
	Cd	0,003	0,04	0,02	0,02	0,01	0,01	0,01	0,01	0
	Fe	1	440	22	24,7	67,4	57,75	3,79	8,91	711

A comparative analysis of the quality of the waters evacuated by the two factories concerning the maximum values measured in the period 1996-1999 shows first of all that the maximum admitted concentration was exceeded at all analysed elements. The maximum values were analysed because at both factories there existed periods of time when the activity was much reduced or even interrupted so that the determinations carried out in that period of time indicated lower values but not due to the pollution degree reduction; thus the average values are not significant. Even if we take into consideration these average values at a simple analysis of data from the table one could find that those ones exceeded too, in the most cases, the admitted maximum concentration values.

By analysing separately the situation of the two factories, the data suggest for the new factory a diminution tendency of the concentrations for the last two years period; but this aspect, as it was underlined before, is the result of activity cessation at this unit and not at all the consequence of some measures for reduction of the pollution degree. A very interesting aspect to be pointed out is that even if the activity was ceased, the acidity of the evacuated waters is maintaining a high degree which means that a large quantity of water is being used in the preservation activity but the purification station does not pass this quantity but it is discharged directly into the river.

Concerning the old factory, the situation is heterogeneous being obvious both the increases of some elements concentration (Cu, Zn) and diminutions (Pb, Cd, Fe) these situations being probably caused by the nature of the processed ore and function time. On the other way, taking into consideration that this unit is not equipped with a purification station the concentrations values should have been much higher than those of the new factory but the

situation seems to be quite inverted, an aspect explained by the production capacity much lower of the old factory than of the new factory.

After synthesizing all data, the conclusion is that at the base of the high load with pollutant agents of the used waters evacuated from the industrial platform stand three categories of factors namely:

- a. *the defective chemical purifications of the used waters* in the case of the decantation station from the new factory whose chemical purification efficiency should be according to the technical norms, of 99%; but the situation is however quite different when this percentage is referred to the heavy metals removal degree whose concentrations in the evacuated waters present considerable exceeding as compared to the authorized values (at copper 4-8 times, at iron 2-3 times and in the case of solid suspensions ~ 2-3 times)
- b. *the diminishing reliability of the equipments* used in this technologic process that leads repeatedly to discharges of technologic solutions with high concentration of pollutants these ones reaching directly in the evacuation circuit;
- c. *the inappropriate collection of cooling waters*, washing waters and meteoric waters due to the fact that the transportation tubing system of the used waters was arranged in diverse phases and there was no unique project of this system that might answer to all requirements of the matter.

DOUBLE NATURE (HYDROTHERMAL-SÉDIMENTAIRE FÉRRIFÈRE ET TERRIGÈNE) DE LA PILE DU GROUPE PALAZU MARE – PROTÉROZOÏQUE INFÉRIEUR (DOBROGEA – ROUMANIE)

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Les forages exécutés dans la partie du Nord de la Dobrogea Méridionale, dans la région Palazu Mare-Cocoșu, ont montré que, sous la couverture sédimentaire (Mésozoïque et Tertiaire), le socle de la Plateforme Moésienne est représenté par trois entités métamorphiques (de bas en haut): (1) **Cristallin de Iași-Palazu – CIP** qui renferme des gneiss migmatiques, granites gneissiques, paragneiss, micaschistes et pégmatis (Ivanovici, Giușcă, 1961; Giușcă et al., 1967), aussi rencontrés (Ivanovici, Giușcă, 1961) dans le soubassement de la Plateforme de Moldavie (Plateforme Est-Européenne). Le CIP a un âge antéprotérozoïque – prékarélien (Giușcă et al., 1967), étant tout semblable avec la formation gneissique prékarélienne du Bouclier Ukrainien. (2) **Groupe Palazu Mare – GPM** (protérozoïque inférieur – karélien) – l'objet du cet article. (3) **Le Groupe Cocoșu – GCo** (Briovérien – Kräutner et al., 1988). Ces trois entités constituent la Nappe de Palazu, charriée (données de forages) le long de Charriage Palazu intra-moésien – cimmerien ancien (Mureșan, 2005, 2006), sur le Groupe des Schistes Verts – GSV (Briovérien supérieur – Mirăuță, 1965, 1969) de la Dobrogea Centrale (Fig.). Le GSV représente la partie septentrionale de la Plateforme Moésienne.

I. GROUPE PALAZU MARE (GPM). Le GPM (500-800 m), qui renferme des roches férifères et terrigènes, a été considéré, par Giușcă et al. (1967) – selon sa pétrographie et l'âge du son métamorphisme régional (données K / Ar = 1777-1620 m.a.), un équivalent de la Série de Krivoi Rog, d'âge karélien (protérozoïque inférieur). La présence de l'andalusite et du sillimanite dans les micaschistes et l'absence du cordiérite montrent que le métamorphisme régional s'est déroulé dans le faciès des amphibolites, autour de 600° C et 4-5 Kb (Giușcă, 1977). Maier et Mișu (1976 et dans Visarion et al., 1979) ont séparé, dans la pile du GPM, deux entités lithostratigraphiques: **PM1 – Complexe inférieur des schistes quartzito-amphiboliques ± magnétite** et **PM2 – Complexe supérieur des micaschistes à andalusite.**

PM1 (500 m, l'épaisseur maxima connue) renferme une suite des roches férifères (décrites par Giușcă – 1977 et Giușcă et al., 1976), représentés principalement par des roches quartzieuses à amphiboles et magnétite (caractérisées par leur texture rubanée, donnée par des minces couches stratiformes quartzitiques, amphiboliques et magnétitiques), dans lesquelles s'intercalent schistes à cummingtonite, biotite et almandine, roches cummingtonitiques-

quartzeuses à magnétite, roches carbonatées à silicates ferrifères (par exemple, roches calcaires à ferrosalite et grandite, dolomites à ferrosalite et magnétite), quartzites ± magnétite et, rarement, des intercalations de micaschistes, paragneiss et amphibolites. Les roches à hématite sont très rares (quartzites à hématite ± magnétite ± antophyllite). À la suite de leurs études pétrographiques, minéralogiques et géochimiques des toutes ces roches, Giușcă et al. (1977) ont admis leur l'origine sédimentaire marine, les sédiments originaires étant représentés par des cherts (silicolites), cherts à magnétite, cherts pistomésitiques, cherts pistomésitiques à magnétite, cherts ankéritiques, cherts pistomésito-dolomitiques, toutes ces sortes pouvant avoir aussi des quantités variables de silicates ferrifères primaires et, assez fréquemment, de limons argileux (hydromuscovite, caolinite) et, parfois, des limons marneux (les deux derniers type étant considérés à l'origine des roches à hornblende). **PM2** (> 300 m) renferme (Giușcă, 1977) des micaschistes (assez fréquemment graphiteux) ± almandine ± andalusite ± sillimanite (les trois minéraux séricitisés), dans lesquels s'intercalent des paragneiss, des quartzites à muscovite et biotite, des quartzites feldspathiques à muscovite et des amphibolites.

II. NOS COMMENTAIRES. (A) Concernant la limite GPM / CIP. Contrairement à toutes les opinions, nous considérons qu'aujourd'hui le CPM est décollé tectoniquement (court charriage?) vis-à-vis de CIP. Ce décollement post-métamorphique (probablement pénécontemporain avec le Charriage Palazu) a écarté les termes basales du GPM. **Nos arguments:** (1) à la base du GPM, il n'y a pas des roches détritogènes (métagrès, métaarcsos, métaconglomérats), des metabasites (métaspilites, métagabbros) et, parfois, des métavolcanites acides, un ensemble connues, en échange, à la base de la pile de la Formation de Krivoï Rog d'Ukraine (Belevtsev, 1968; Smirnov, 1976) et, d'ailleurs; à la base des piles du Protérozoïque inférieur à minéralisations ferrugineuses, logées dans quelques anciens boucliers du monde; (2) entre les séparations lithologiques du GPM et la limite avec le CIP il y a une discordance angulaire (autour de 10° – voir les coupes géologiques (Maier, Miha, 1976 et dans Visarion et al., 1979); (3) la croissance visible, vers le SSO, de l'épaisseur de la pile du GPM (observée par Maier, Miha, 1976); (4) immédiatement, sous le GPM, les roches du CIP sont partiellement rétro-morphisées (Maier, Miha, 1976). Mais ces observations n'oblitérent pas le fait que GPM est formé primordialement dans un bassin sédimentaire, installé sur les métamorphites archéens du CIP. **(B) Concernant la pile du PM1.** (1) Les actuels rythmes des roches ferrifères (comme d'habitude, submillimétriques, millimétriques, centimétriques) expriment l'aspect métamorphique de l'alternance primaire (prémétamorphique) des minces couches stratiformes différentes par leur minéralogie et par leur géochimie. Ainsi, se sont formée, pendant la blasthèse, par exemple, les bandes

stratiformes à silicates riches en fer (cummingtonite, fërrosalite, grandite, hornblende ferrifère etc), les minces couches de magnétite etc. Selon Maier & Mihi (1976), l'orientation générale de la stratification des roches du GPM est ONO-ESE / 35-40° SSO (mesurée sur les carottes orientées). (2) Dans le PM1, le magnétite prédomine nettement sur le hématite, fait que nous l'expliquons par le haut degré du métamorphisme régional du GPM: les oxydes ferrifères hydratés primaires, pendant la blasthèse, ont recristallisés préféablement sous forme de magnétite, plus stable dans les faciès des amphibolites à sillimannite du GPM. Les roches à magnétite du PM1 provoquent une intense anomalie magnétique de la région Palazu Mare (Airinei, 1951), situation ressemblante avec celles du gisement Kursk, aussi plus intensivement métamorphisé et connu aussi par la grande anomalie magnétique qui l'accompagne. En échange, dans le gisement Krivoï Rog, plus faiblement métamorphisé, le hématite domine par sa fréquence le magnétite. (3) La pile ferrifères, renfermée dans le PM1, c'est du même type rencontré dans les piles ferrifères rubanées (du type « Iron banded Formation » – BIF) du Protérozoïque inférieur, logées dans quelque ancien bouclier du monde. Par conséquent, nous proposons pour le PM1 une autre dénomination plus représentative: « **Formation ferrifère rubanée de Palazu Mare** » (en anglais: « **Palazu Mare Banded Iron Formation** »; en roumain: « **Formațiunea feriferă rubanată de Palazu Mare** »). (4). Étant situé au-dessus de soubassement archéen (prékarélien – représenté par le CIP), cette formation peut-être mise en parallèle du point de vue stratigraphique, par exemple, avec: (a) la Série de Krivoï Rog (Giuscă et al. (1967), étant aussi disposée sur l'Archéen (Prékarélien); (b) avec la pile ferrifère de l'Huronien inférieur du Bouclier canadien, étant la première entité ferrifère rubanée du Protérozoïque inférieur, située au-dessus de l'Archéen (Temiskaming et Keewatin) du ce bouclier. Nous remarquons que la pile du GPM est plus métamorphisée que la Série de Krivoï Rog (métamorphisée principalement dans le faciès des schistes verts – Belevtsev, 1968 ; Smirnov, 1976). (C) **Concernant la pile du PM2.** (1) Cette entité est principalement terrigène. (2) Pour le PM2, nous proposons un autre dénomination, qui indique sa principale origine: « **Formation terrigène de Palazu Mare** ».

III. GENÈSE DE LA PILE PRIMAIRE DU GPM. (A) Nos arguments en faveur de l'origine hydrothermal-sédimentaire de la pile du PM1 (en dehors des amphibolites magmatogènes et des roches terrigènes, intercalées dans le PM1). (1) Puisque les quartzites (couches indépendantes, ou des bandes minces, présentes dans la majeure partie des roches ferrifères) ont des structures mosaïquées (pavimenteuses), nous pouvons conclure qu'il s'agit de gels siliceux métamorphisés et que l'état gélique parmi les roches primaires de l'ensemble ferrifères, était très répandue, situation spécifique pour les gisements

hydrothermal-sédimentaires. (2) Les roches carbonatées à silicates ferrifères (sûrement métamorphiques) $\pm$ magnétite (par exemple, roches calcaires à ferrosalite et grandite $\pm$ magnétite, dolomites à ferrosalite et magnétite) étaient primairement ferrifères, selon nous, de nature hydrothermal-sédimentaire. Un exemple nous l'avons dans le Dévonien moyen épimétamorphique du Massif Poiana Ruscă (dans la partie du NO des Carpates Méridionales); là, il y a des gisements concordants (Teliuc, Ghelar, Vadu Dobrii, Ruschița), d'origine hydrothermal-sédimentaire marine (Kräutner, 1964, 1977), constitués principalement par une association de sidérites, ankérites, paraankérites, ferrodolomites, dolomites faiblement ferrifères, quartzites à structure mosaïquée (gels siliceux métamorphisés), roches dans lesquelles sont, parfois, présents le magnétite et les silicates ferrifères. (3) L'origine continentale du fer, transporté dans les eaux marines et, ultérieurement, déposé sous formes de gisements colossaux ferrifère du Précambrien inférieur, n'est pas vraisemblable, tenant compte de: (a) les formations archéennes renferment presque seulement des roches léucocrates (gneiss, granitoïdes etc), donc à teneur très réduite en fer; (b) l'absence de l'action protectrice des acides humiques (non-existants pendant le Protérozoïque inférieur), fait impossible le transport du fer, en grandes quantités et à longues distances, dans les eaux marines à électrolytes.. **B. Schéma des processus génétiques.** (1) Les vecteurs transporteurs du fer ont été représentés par les hydrothermes en état colloïdale. (2) La charge colloïdale des hydrothermes était constituée prédominant par la silice et par les oxydes hydratés de fer, aux quels, parfois, s'ajoutaient des bicarbonates de fer, de calcium et de magnésium. (3) Le contact avec les électrolytes des eaux marines et la diminution de la température des hydrothermes ont déterminé la floculation des leurs charges minérales, les flocons restant un temps dans les eaux marines; constituant une suspension, comme un « nuage », très près du fond de la mer, qui a créé un milieu assez différent vis-à-vis des eaux marines « normales », ayant des autres compositions chimiques, températures, valeurs du pH etc. (4) Pendant les processus du dépôt des flocons a intervenu une certaine différenciation selon leurs propriétés physiques et chimiques, se formant des couches superposées (minces ou grossières), différentes par leur compositions, ainsi résultant le rubanage primaire de la formation ferrifère. (5) Comme d'habitude, les volumes des apports hydrothermal-sédimentaires ont dépassé nettement les volumes des apports terrigènes, étant une indication que les concentrations ferrugineuses ont été déposées loin de rivage du bassin marin originaire. Les rares intercalations de roches terrigènes (micaschistes, gneiss) de la PM1 correspondent aux périodes d'interruption de l'activité hydrothermal-sédimentaire. (6) Pendant la formation tant de la pile du PM1, que de la pile du PM2, ont pris naissance des rares roches magmatogènes basiques concordantes (probablement, coulées et/ou métaépicroclastites basiques), représentée

aujourd'hui par les intercalations d'amphibolites. **C. Conclusions.** (1) La pile du PM1 est principalement de nature hydrothermal-sédimentaire ferrifère, dont l'épaisseur (environ de 500 m) représente plus que la moitié de l'entière grosseur connue du GPM (800 m). (2) La pile du PM2 (> 300 m) est principalement terrigène (3) La haute intensité du métamorphisme régional, a déterminé la transformation complète des tous les composants primaires de la pile du GPM, par réactions métamorphiques et par la récrystallisations. Dans le PM1, la blasthèse a amplifié les textures rubanées primaires, qui expriment la stratification initiale.

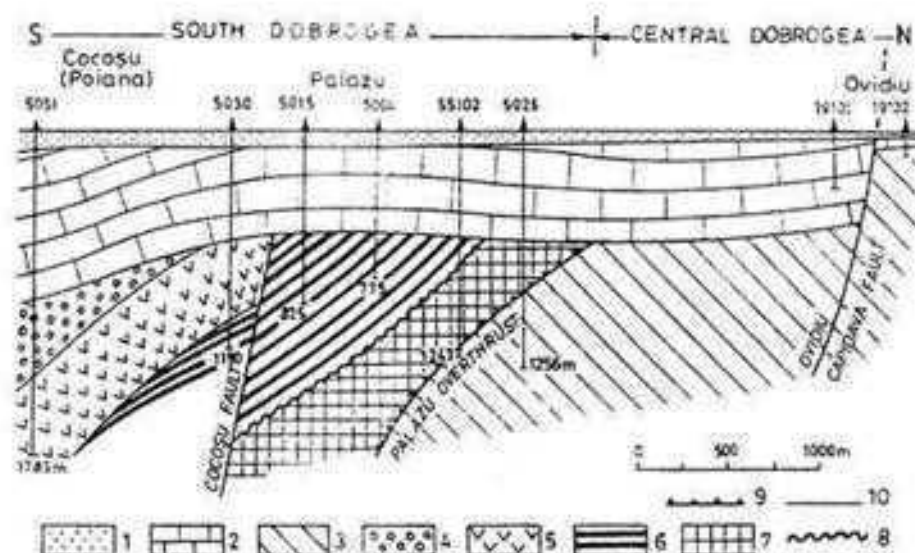


Fig.1. Coupe géologique Cocosu-Palazu Mare-Ovidiu (partiellement selon Kräutner et al., 1988; selon Mureșan, 2005: la Nape de Palazu, la limite Dobrogea Méridionale / Dobrogea Centrale et le décollement du GPM). 1, Crétacée supérieure et Tertiaire; 2, Jurassique moyen et supérieur; 3, 4, 5, 6, 7, Plateforme Moésienne: 3, Groupe des Schistes Verts (Briovérien supérieur); 4, 5, 6, 7, Nape de Palazu: 4, 5, Groupe Cocosu (Briovérien – 4, Formation supérieure détritique; 5, Formation inférieure spilitique); 6, Groupe Palazu Mare (Protérozoïque inférieur); 7, Cristallin de Iași-Palazu (Archéen); 8, Contact de décollement du Groupe Palazu Mare; 9, Charriage Palazu; 10, Faille.

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GISEMENT ALTÎN TEPE (PROTÉROZOÏQUE MOYEN) – UN CAS DE TRANSITION DU TYPE SCANDINAVE VERS LE TYPE LAHN-DILL (DOBROGEA – ROUMANIE)

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Gisement Altîn Tepe (les plus importants ouvrages concernant ce gisement: Nițulescu et al., 1967 – constitution minéralogique du minéral; Gurău, 1970 – microtectonique; Ianovici et al., 1971 – statistique des éléments majeurs; Mureșan, 1969, 1972 – microtectonique, litostratigraphie, genèse; Popescu, 1975, 1977 – minéralogie, métalogenèse; Berbeleac et al., 1985 – rétrogenèse du minéral) est logé dans la pile mésométamorphique du **Groupe Altîn Tepe (AT)**, qui affleure dans la partie septentrionale de la Dobrogea Centrale, dans une fenêtre tectonique (Mureșan, 1971), sous le Charriage Istrien du **Groupe des Schistes Verts** (du Briovérien supérieur) – **Fig. 1**. Les deux unités sont limitées par la **Faïlle Peceneaga-Camena (FPC)**.

Groupe Altîn Tepe renferme une pile (> 2000 m), qui, dans ses séquences terrigènes, a un caractère primaire de **flysch** (Mureșan, 1971, 1972), du type arénite-siltite. La pile de l'AT a été mésométamorphisée régionalement dans le subfaciès staurotide-quartz du faciès des amphibolites à almandine (Giușcă et al., 1967), pendant le Protérozoïque – cf. aux âges K/Ar de 696-711 m.a. (Codarcea Dessila et al., 1966; Giușcă et al., 1967). Puisque le rétrogenèse est répandue dans l'AT (Berbeleac et al., 1985; Nedelcu & Gridan, dans Nedelcu et al., 1987, 1988; Mureșan, 2004, 2005), c'est très possible que ces chiffres représentent des rajeunissements partiels, ainsi que l'âge du métamorphisme protérozoïque primordial de l'AT est sensiblement plus grand. **I. Lithostratigraphie du Groupe Altîn Tepe.** L'AT est divisé en quatre formations lithostratigraphiques (Mureșan, 1971, 1972) – **Fig. 1: Les Formations AT1** (> 500 m), **AT3** (850-1250 m) et **AT4** (> 350 m) sont terrigènes (paragneiss plagioclasiques, micaschistes, quartzites), ayant un caractère flyschoides. Dans l'AT3, s'individualise **Le Niveau Valea Minei – NVM** (50-200 m d'épaisseur) – des roches terrigènes, qui logent des minces sills de métagabbros. Dans l'AT4 il y a aussi des rares et minces sills de métagabbros. Dans l'AT4, est logé le **Gisement Altîn Tepe**. **La Formation AT2** (350-550 m) englobe principalement des paraamphibolites et des orthoamphibolites, qui constituent des anciens sills (l'épaisseurs maxima: 50 m) – Mureșan, 1972, 2004). **II. Tectonique synmétamorphique du Groupe Altîn Tepe.** Les mésométamorphites de l'AT constituent un homocline (orienté environ de N 45° O / 65° SO) à descendance normale vers le SO (**Fig. 1**) affecté par des plis synmétamorphiques (du type “drag-folds” – aussi présents dans le minéral

du Gisement Altın Tepe), qui indiquent un puissant plongement axial (environ de 25°-30°) de la structure B vers le SE (Mureşan, 1969, 1972). **III. Traits principaux du Gisement Altın Tepe (GisAT).** (1) Dans ce gisement, les sulfures (principalement la pyrite) prédominent nettement sur la magnétite. (2) Le GisAT est formée par cinq corps principaux et quelques corps moins importants (« lentilles satellites »), tous disposés aux différents niveaux de l'AT4 – Fig. 2. (3) Les corps minéralisés sont fuseauforme-lenticulaires, dans l'exploitation minière, dénommés « lentilles », parce que, dans le plan horizontal, ces corps présentent des formes lenticulaires (allongées NO-SE), terme déjà naturalisé dans la littérature. Cette forme des corps minéralisés est unique parmi les gisements hydrothermal-sédimentaires connus dans notre pays. (4) Tous les corps minéralisés sont concordants avec la schistosité de stratification des roches métamorphiques encaissantes et, vers NO et SE (en plan horizontal), s'effilent et s'endentent facialement avec les schistes voisins. Les corps minéralisés présentent un puissant plongement (25-30°) vers SE – Fig. 3 (avec leurs axes longs), parallèlement avec la structure B des métamorphites de l'AT (Mureşan, 1969, 1972). Les travaux miniers, faits jusqu'à 800 m sous le relief actuel (le Sommet Altın Tepe = 320 m), ont montré la continuité en profondeur des ces corps minéralisés. (5) La Lentille I (en plan horizontal: l'épaisseur maxima = 80 m et la largeur maxima = 18 m), la L II (12 m / 120 m); la L III (6-7 m / 120 m), et la L IV (2-3 m / 45 m) sont constituées en majeure partie par de minéral massif (parfois, à minces intercalations de minéral disséminé et de roches terrigènes). La Lentille V et les lentilles satellites englobent principalement de minéral disséminé. (6) Dans la sorte massif on a distingué un type pyriteux et un type magnétitique à oligiste (15-20 % du volume des lentilles à minéral massif). (a) Le minéral pyriteux (pyrite 45-70 %) a comme trait principal une structure « porphyrique », donnée par sa matrice pyriteuse finement grenue, dans laquelle s'individualise des porphyroblastes de pyrite (0,5-3 mm), aux quelles, rarement, s'ajoutent des porphyroblastes (< 1,5 mm) et grains (0,3 mm) de magnétite (0-15 %) La matrice est constituée par des grains (comme d'habitude < 0,1 mm) presque isométriques de pyrite, allotriomorphes et hypidiomorphes (souvent fissurés), parmi lesquels s'insinue le quartz (5-10 %), la barytine (8-10 %), la chalcopirrite (4-7 %), parfois la blende (0,5-1 % et la galène (< 0,5 %). Comme d'habitude, le minéral est rubanné, comme résultat de l'alternance des bandes à constitution minéralogique différente, ou bien à l'alternance du minéral avec les roches terrigènes; parfois, on remarque (au microscope) des bandes pyriteuses parallèles avec la stratification, dans lesquelles le « ciment » de la matrice est différent, étant constitué principalement par chalcopirrite, ou de quartz et barytine, ou de blende. Toutes ces situations expriment la stratification primaire du minéral. (b) Le minéral magnétitique a une structure granulaire, parfois porphyrique et une texture massive, ou

rubannée, ou schisteuse (dans les variétés riche en oligiste – jusqu'à 20-25 %) et contient, à côté de magnétite (grains et porphyroblastes, parfois partiellement martitisés); l'oligiste (les deux minéraux = 60-75 %) et, assez fréquemment, des petits grains ou porphyroblastes de pyrite (2-5 %), aux quelles s'ajoutent la barytine (8-10%), le quartz (5-15 %), le muscovite (2-4 %); la matrice est plus pauvre en chalcopryrite, blende et galène que celle du type pyriteux. Les travaux miniers ont relevé que, les parties du NO des corps à minéral massif (Lentilles I, II, III, IV) sont constituées (sans exceptions à tous les horizons miniers) par le type magnétitique (Fig. 4). Parfois, surtout dans le cas de la Lentille I, le minéral magnétitique se développe aussi à la partie supérieure (vers au bout du NO du ce corps), ainsi résultant un « capuchon » fait en minéral magnétitique, qui couvre, vers le NO, le minéral pyriteux du ce corps minéralisé (Fig. 4). **Entre les deux sorts de minéral massif il y a des transitions assez graduelles**, exprimées tant par la coexistence de la pyrite et de la magnétite, que par l'alternance des bandes magnétiques avec celles pyriteuses – Fig. 5. (c) **Le minéral disséminé** constitue soit des lentilles indépendantes (Lentille V et les corps satellites), soit des intercalations dans les corps à minéral pyriteux massif, ou les zones périphériques des ceux-ci. Ce type est représenté par des schistes quartzeux (quartz 25-60 %) muscovito-chloriteux (provenant du biotite)-pyriteux (pyrite 10-30 %) à chalcopryrite (<1 %) et barytine (<2%); le magnétite c'est très rare. (c) Tant dans le minéral disséminé, que dans les minéral massif, les roches quartzieuses présentent assez fréquemment des structures mosaïquées, exprimant, selon nous, l'aspect métamorphique de l'état initiale géliforme des dépôts siliceux primaires. (d) Nous remarquons que les quantités assez importantes de barytine dans les deux types de minéral massif et la présence constante de ce minéral dans le minéral disséminé représentent un trait distinctif pour le GisAT, vis-à-vis d'autres gisements de sulfures hydrothermal-sédimentaires métamorphisés connus dans la Roumanie. (7) **Quelques indications concernant la métamorphose régionale du minéral du GisAT.** À côté de données d'ordre régionale et de celles de la géologie du GisAT, la structure intime du minéral présente quelques indices en ce sens. (a) **Les ombres de pression (pressure shadows)**, rencontrées assez fréquemment autour de la pyrite et de la magnétite, représentées par des individus allongés de quartz, ou par des lamelles de chlorite, disposés quasi-perpendiculairement sur les faces cristallographiques opposées de la pyrite ou de la magnétite, respectivement orientés parallèlement avec la schistosité du minéral. (b) **L'inclusions poikiloblastiques**, par exemple, de la pyrite et de la magnétite dans les grenats. (c) **L'association des minéraux métallifères** avec des minéraux rencontrés fréquemment dans les roches métamorphiques (chlorite – provenant du biotite, muscovite, grenat, épidote etc). (d) **Le plissement du minéral** sous forme de plis du type « drag folds » (Fig. 5), aussi connus dans la pile de l'AT.

IV. La genèse du gisement Altin Tepe. Auparavant, nous avons argumenté la genèse hydrothermal sédimentaire du GisAT (Mureşan, 1969, 1972) et la métamorphose régionale de celui-ci. Aujourd'hui, tenant compte: (a) de contexte lithostratigraphique de la pile de l'AT (terrigne à intercalations puissantes d'amphibolites magmatogènes basiques); (b) de développement du minéral magnétique dans les parties du NO des corps à minéral massif (Lentilles I, II, III, IV – Fig. 4) et les transitions assez graduelles entre les deux types de minéral massif, nous pouvons préciser que les concentrations des sulfures du ce gisement sont, à l'origine, hydrothermal-sédimentaires du type scandinave, qui présentent des transitions vers le type oxydique ferrifère du type Lahn-Dill. Les causes primaires de la coexistence du type scandinave avec le type du Lahn-Dill. (1) Quoique les deux types sont contemporains, ayant à l'origine les mêmes hydrothermes, chacun type est différent en ce qui concerne le contenu en soufre et le contenu en métaux colorés (Cu, Pb, Zn). (a) Ainsi, la transition primaire du faciès à sulfures vers le faciès oxydique ferrifère exprime le fait que le soufre n'a pas été en quantité suffisante pour lier le fer entier sous forme de sulfure; c'est très intéressant, que cette situation s'est répété pour chaque corps à minéral massif. (b) Le teneur pauvre en Cu, Pb et Zn du minéral magnétique, peut être expliquer par les distances plus grandes du celui-ci vis-à-vis de zone où débordaient (dans les eaux de la mer) ces hydrothermes, les sulfures de Cu, Pb et Zn se précipitant préférentiellement plus rapidement, dans les zones à sulfure de fer.

Nous faisons l'observations que des transitions vers le type Lahn-Dill nous les pouvons observer aussi dans quelques cas des gisements ferrifères (du Dévonien moyen de Poiana Ruscă), développés dans le faciès à carbonates (sidérites, ankérites etc) du type Teliuc-Ghelar (types devenus classiques par les études de Kräutner, 1964, 1974, 1970, 1977, 1996), qui passent vers les minerais magnéto-hématitiques (nous les considérons du type Lahn-Dill) associés (par exemple, Teliuc Est, Pădurea Oraşului, Nicolson).

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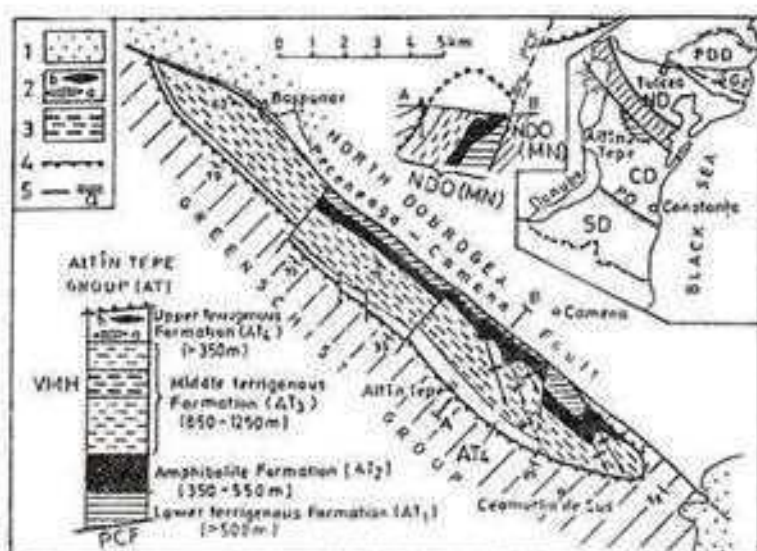


Fig. 1

Fig. 1 - Esquisse tectonique de la région Altin Tepe. 1, Crétacée supérieur; 2, AT4 (a. Métagabros; b. Minéral syngénétique); 3, VMH, Niveau Valea Minei (roches terrigènes et métagabros); 4, Charriage Istrien; 5, Faille Peceneaga-Camena (a. tronçon rejoué post-crétaïque supérieur). Abréviations: SD, Dobrogea Méridionale; CD, Dobrogea Centrale; PDD, Dépression Prédobrogeenne; PO, Charriage Palazu; PCF, Faille Peceneaga-Camena; SGF, Faille Sfântu Gheorghe; NDO, Orogen Nord-Dobrogeen; (MNO, Nappe de Măcin du NDO).

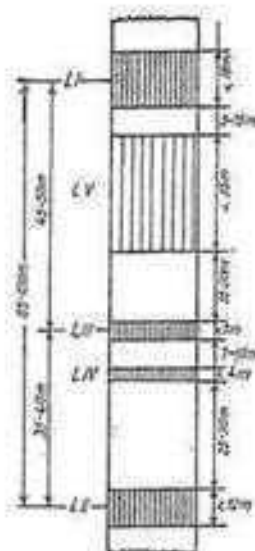


Fig. 2

Fig. 2 - Colonne lithostratigraphique synthétique du Gisement Altin Tepe. L I, L II, L III, L IV, lentilles à minéral massif; L V, lentille à minéral disséminé.

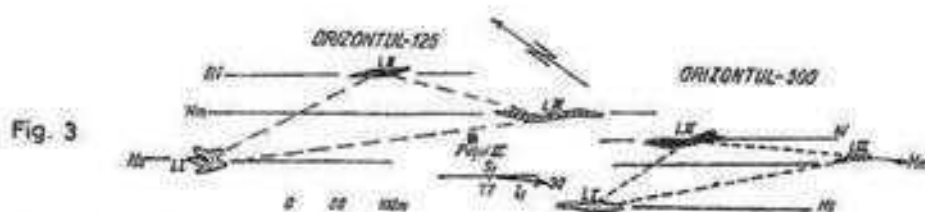


Fig. 3

Fig. 3 - Situation des lentilles principales à minéral massif à l'Horizon -125 et à l'Horizon -500. H1, Niveau lithostratigraphique inférieur de la L I; H2, Niveau lithostratigraphique moyen de la L II; H3, Niveau lithostratigraphique supérieur de la L I; S1, position moyenne de la schistosité de stratification et la position de la linéation moyenne parallèle avec la structure symmétrique B. Le plongement des lentilles vers SE détermine le déplacement en profondeur du triangle des celles-ci par rapport à la verticale du Puits III.

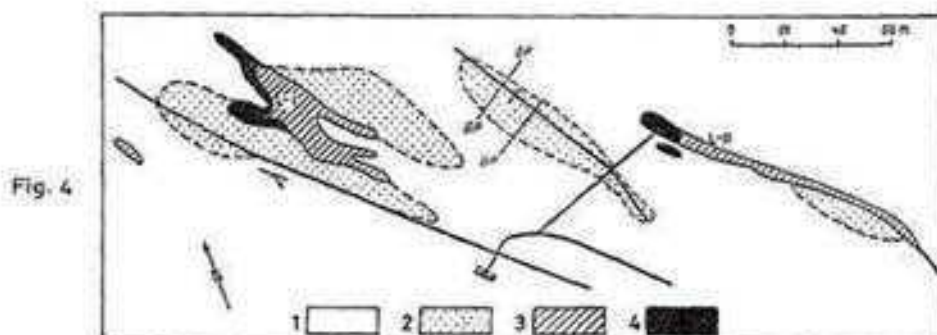


Fig. 4

Fig. 4 - Esquisse des corps minéralisés à l'Horizon 250 m (selon Gurău, 1970). 1, Schistes terrigènes; 2, Minéral disséminé; 3, Minéral massif de sulfures; 4, Minéral magnétique à oligiste.

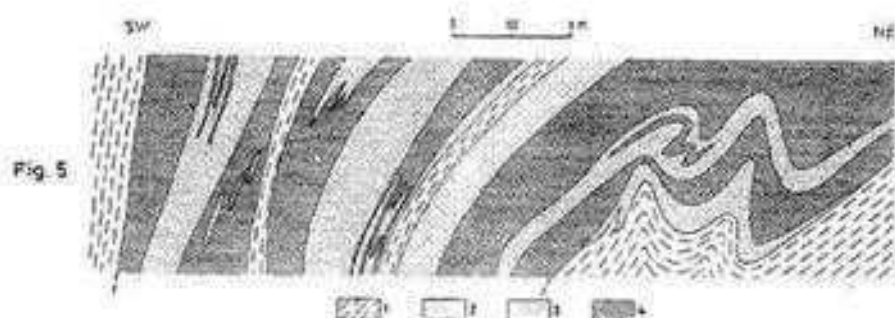


Fig. 5 – Vers la partie du NO de la Lentille II (dans le front de l'abatage de l'Horizon ~350), dans la zone de transitions entre le minéral pyriteux et le minéral magnétitique. 1, Schistes muscoviteux-quarzeux à biotite chloritisé; 2, Schistes quartzeux pyriteux; 3, Minéral pyriteux; 4, Minéral magnétitique à oligiste. L'ensemble est affecté par de plis symmétamorphiques du type « drag-folds ».

THE OIL HYDROCARBON BIODEGRADATION CORRELATED WITH REHABILITATION POSSIBILITIES OF A POLLUTED ECOSYSTEM

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The importance of the biodegradation phenomenon has been noticed firstly by Seyer Chibnall (1933) on the grounds of high frequency of active soil microorganisms and their capacity of stocking synthesized plant hydrocarbon (with C_7H_{16} - $C_{35}H_{72}$) or other insect produced waxes.

The microbial crude oil degradation in natural eco-systems is a specific case of microorganism activity (clastic hydrocarbon bacteria, Zarnea, 1994). It is a complex process the evolution of which depends on the nature and relative proportion of different oil constituents on the nature of specific microorganism characteristic to those environments and on a series of environmental factors influencing their activity

The actual soil condition is firstly a consequence of its past formation. The microorganisms (bacteria, cyan bacteria, lees and fungus species) are those ensuring the continuous circuit of major and minor elements in nature; they can bring about through geochemical circuit the main elements for life development. By analogy it has been noticed that they are able to clean a crude oil polluted environment through natural degradation of hydrocarbons.

Thus, the anaerobe bacteria isolated in ground waters, developed in cultures are capable of reducing sulphates, albumin decomposition, cellulose, lactic and acetic acid with forming gas compounds such as CH_4 , CO_2 , NH_3 , H_2 , N_2 and H_2S , and other are able to catalyze the oxidation of aromatic or paraffin hydrocarbons.

Although the crude oil pollution phenomenon is frequent in soil, as in rivers, the focus is mainly on marine environment where massive and impressive dumping is made, causing brutal effects on organisms and environment itself.

Oil is known to be a set of hydrocarbon degraded at different degrees by microorganisms (Zarnea, 1994):

1. Aliphatic fractions (saturated) represented by alkenes iso- and cyclic alkenes The linear molecules are more likely exposed to microorganisms
2. The aromatic fraction represented by benzene like compounds, resistant molecules to decomposition

3. The asphalted fraction which includes complex structured compounds, these are resistant to biodegradation

A key issue is that yearly 3.2 billion tones of oil are wiped out the oceans through different ways. From an ecological point of view there are two types of pollution: one is the slow, permanent, unperceivable eliminations and the others are the mass entropic contaminations from the seashore oil plants from contaminated rivers, and from industrial and urban emissions. Like wise, one should add the leaks from marine extraction platforms and especially out shore discharges of waste oil waters from the ships oil tanks.

At the atmosphere pollution one can add the residence in the atmosphere of 600 000 tones of hydrocarbons initially existing in ores containing volatiles aromatic compounds (1400 tones/a year of benzene pirent) generally cancer causing and 50000 t/year natural leaks through cracks and diffusion (Wilson & Miller, 1974).

The degradation process takes place in two stages:

- The first critical stage, with a time span of a couple of hours to several days, corresponds to rapid exposure of oil on a large scale of marine environment is associated with physical processes (evaporation, dissolving, mixing) of first rank in the biodegradation process evolution

In these stages the pollutant separates in two different ways (physical and chemical):

- The surface layer of the light fractions forming a shinny layer at the water surface. It has multiple negative effects because it alters the wave dynamics, slows down water evaporation and oxygenation retains chemical pollutants (detergent, heavy metals and even microorganisms). Under the action of atmospheric currents aerosols may form and be spread on large distances and finally lay down on the crops.
 - The oil track containing the water flow undergoes an emulsion treatment process characteristic to aquatic ecosystems. This is a key process in biodegradation consisting of two stages: firstly the oil-water emulsion resulting at the surface and is spread by waves and marine currents on large distances and secondly the water-oil emulsion consisting of heavy fraction of crude oil and a big quantity of water (80%).
- The second stage of hydrocarbon degradation develops in two different ways:
 - Bio-degradation is done in aquatic ecosystems especially by bacteria, adding fungi and some algae. Like wise some animal organisms (annelids, polikets) can degrade a part of the absorbed hydrocarbons through activating a special enzyme.

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A BIOGEOCHEMICAL STUDY OF LAKES IN BUCHAREST CORRELATED WITH POLLUTION PHENOMENON

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For this approach we must take into account the lake formation in Bucharest as well. The lakes in Bucharest are part of the Campia Romana (Romanian Plain), being formed in depressions as a result of settling along the river banks. Beside these types of lakes in Bucharest, there are also artificial lakes for recreation.

The water supply for these lakes is done through precipitations and fresh running streams where the springs are not clogged and at most of the lakes the water excess flows through emissaries (the Pantelimon lake)

The lakes were formed initially as oligotroph aquatic basins and progressively became eutrophic as the sediments were building and the nutrients increased on one hand and the increase of water volume, on the other hand. In Table 1 are given the water tests data for Morii, IOR and Herastrau lakes (1995) at different concentration for the total amount of salts.

Table 1-The concentration of different ions in Bucharest lakes

Ions (cations/ anions)	The MORII Lake (Crangasi)	The IOR Lake (Balta Alba)	The Herastrau Lake
K ⁺	0,85	2,16	1,01
Na ⁺	31,88	13,65	0,37
Ca ²⁺	2,46	4,87	0,50
Mg ²⁺	0,56	1,18	1,23
Cl ⁻	46,21	22,14	5,064
SO ₄ ²⁻	5,68	19,33	9,09
NO ₃ ⁻	1,54	2,27	0,74
CO ₃ ²⁻	7,26	2,72	0,12
(Fe,Al) ₂ O ₃	3,70	0,30	0,589
SiO ₃ ²⁻	2,50	1,50	0,12
Conc. of total salts (g/l)	111,86	70,12	18,71

The I.O.R lakes are supplied by underground waters and are loaded with sulphates (SO_4^{2-}) and chlorine (Cl^-). The concentration of salts from the other lakes is due to the supply of salts of contact waters, after each rainy season, and due to the evaporation phenomenon from the draught season as well.

To be able to observe the variation of salt concentration in the rainy season compared to the draught season the result obtained are shown in Tab. 2 and 3.

Table 2- The average of water tests of Bucharest lakes

lakes in the rainy season	
Ioni (cationi/anioni)	Media după sezonul ploios (1994) g/l
K^+	0,247
Na^+	9,119
Ca^{2+}	8,767
Mg^{2+}	15,907
Cl^-	16,471
SO_4^{2-}	6,541
NO_3^-	-
CO_3^{2-}	6,514
NH_4^+	0,014
H_2SiO_4^-	-
PO_4^{3-}	4,490
H_2S	(before season) 0,59

Table 3- The water tests of Bucharest

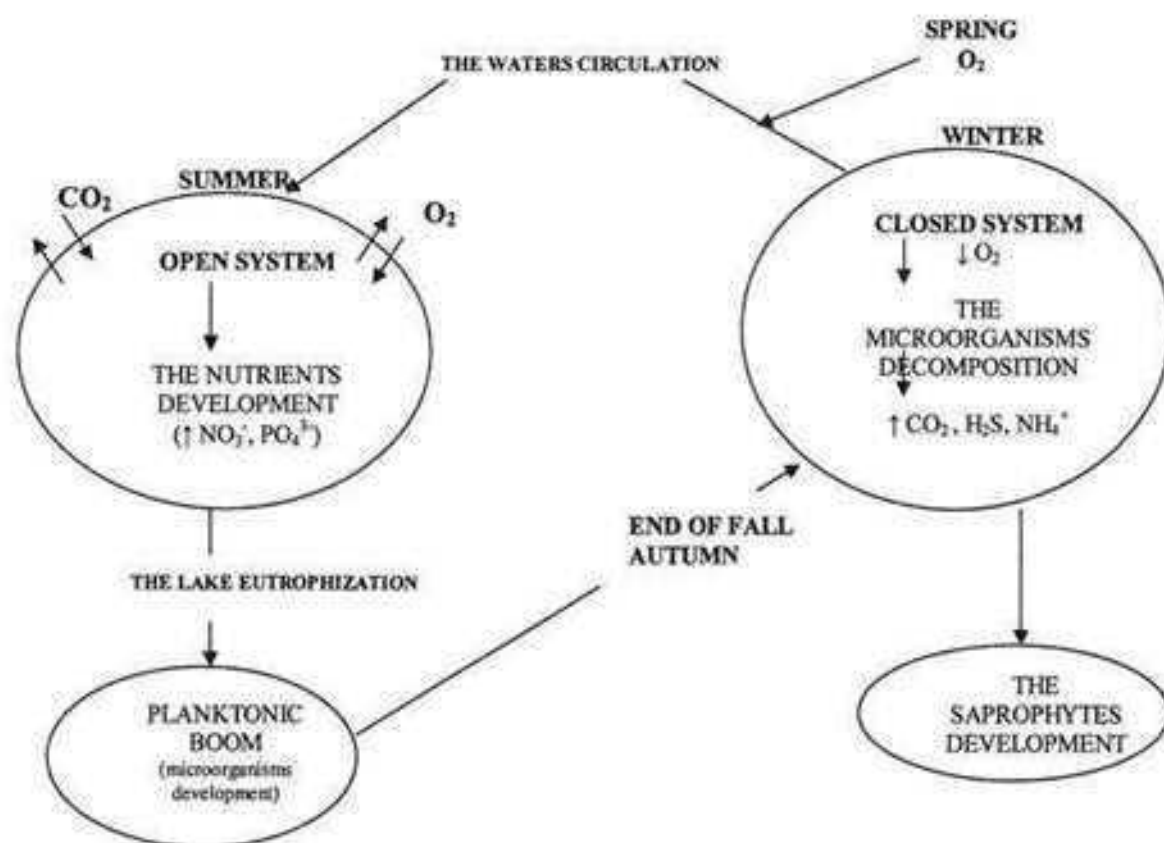
Ioni (cationi/anioni)	Lacul IOR (1994) g/l	Lacul Pantelimon (1994) g/l
K^+	3,565	1,832
Na^+	10,652	5,313
Ca^{2+}	0,150	2,431
Mg^{2+}	14,522	6,945
Cl^-	39,524	10,244
Br^-	0,077	0,397
SO_4^{2-}	8,025	14,081
CO_3^{2-}	0,069	-
H_2S	0,130	-
$\text{H}_2\text{SiO}_2^{4-}$	0,080	0,119

The salinity of Pantelimon lake decreases a lot, probably because of the many fresh water springs existing under the loess layer. Through tests comparison it can be observed that the salinity of the IOR lake is increased a lot due to its reduced area. Thus, in 1983, the water of this lake had a total salts concentration of 40g/l, and in a couple of years in the Eastern part of the lake, in the unplanned area, there was registered a total salt concentration of 52.50 g/l.

In the Northern Bucharest lakes, during summer, the organic matter is relatively abundant. In autumn, due to decreasing temperature, water currents appear (convection currents) favoring flowing so that there are planktonic booms decreasing in winter. When the lake freezes in winter, it negatively affects some organisms existence (the ice layer prevents the water oxygenation and the snow layer stops light penetration), in this period, O_2 dissolved

in water is consumed in the decomposition processes, and CO_2 and NH_4 concentration in water increasing.

In spring the flow phenomenon appears again in lake waters, which increases the atmospheric O_2 concentration, so that favorable conditions to nutrients increasing are created and waters overflow.



Thus, the nutrients concentration in lakes does not naturally undergo some rapid or permanent alterations which make a natural, stable, life enhancing balance.

The fresh water lakes, like Bucharest lakes have a very different micro-biotic which includes all microorganisms categories: eubacteria, actinomicete, cyanbacteria, micro fungi, micro algae, and protozoors.

The bacteria are mostly Gram negative and mobile (80-95%) of a very different morphology.

The Bucharest lakes display immobile bacteria generally, bacilli included. The free one being generally allophone, passing from a place to another like atmosphere .Water is a good dispersion environment, favoring microorganisms circulation too.

The bacteria number and their vertical distribution register high season variations. In the clean lakes, their number is maximum at maximum phytoplankton production (in spring, end of summer and beginning of autumn); summer influencing through the thermal

stratification of lake water. In polluted lakes, the saprophytes grow in autumn and in winter when the O_2 concentration increases the anoxic reducing conditions and there is reduction of SO_2 at S_2 forming thus H_2S .

MAGNETIC SUSCEPTIBILITY AS A PROXY FOR HEAVY METALS IN THE STREET DUST FROM THE BAIA MARE TOWN

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Abstract. The present work concerns the application of magnetic susceptibility measurements as a proxy for heavy metals pollution of street dust from Baia Mare.

Introduction. The Baia Mare region of Northern Romania has historical air, water and soil pollution with heavy metals resulting from several centuries of an active polymetallic mining and refining industry connected with the ore deposits from the neighboring Oas-Ignis volcanic mountains (Popescu et al., 1999, 2000). In the eastern part of Baia Mare town, there are two smelting factories, Romplumb and Cuprom. The main industrial activity at Romplumb is processing polymetallic ores from nearby mines to obtain lead ingots. For internal needs the site includes an oxygen factory and iron and steel cast facility. Cuprom plant produces electrolytic copper and selenium, tellurium, gold and silver as secondary products. The plant has facilities to obtain sulfuric acid from metallurgical gases and produces lead oxides and lead sheets as secondary products. The main emissions from these plants contain particulate matter with Pb, Cd, Cu, Sb, As and flying ashes. In the western part of city there are many mining dumps and flotation centers.

Links between heavy metals and magnetic minerals were already postulated in the 1980's (Thompson and Oldfield, 1986). Later studies have found significant correlations between heavy metal concentrations and low-field magnetic susceptibility (e.g. Hanesch et al., 2001). This correlation is based on the adsorption of heavy metals on magnetic iron oxides.

We have measured magnetic susceptibility and heavy metal content from street dust for 61 samples from the Baia Mare town and compared eastern industrial part with other part of the town.

Sampling. The street dust samples have been taken from the air-soil interface from the main crossroads of the industrial areas located in the eastern and western part of town. For comparison, some dust samples have been taken from the residential area situated between the industrial areas.

Magnetic data. Magnetic measurements were performed in the Paleomagnetic Laboratory of the University of Bucharest. Magnetic properties reflect the type, amount, and magnetic grain

sizes of magnetic minerals in geological materials. We measured several rockmagnetic parameters:

(1) magnetic susceptibility - measured for all samples low (Klf) and high (Klf) frequency - the measurements were done with a Bartington MS2B magnetic susceptibility system with two operating frequency 0.465 Hz and 4.65 Hz; (2) anhysteretic remanent magnetization (ARM) - imparted using an alternating field with peak intensity of 100 mT and bias field of 0,05 mT, and (3) isothermal remanent magnetization (IRM). ARM and IRM were measured with JR5 spinner magnetometer. After measurement of ARM the IRM was first imparted in a 2T field (SIRM) and then in opposite direction in a field of 0.3T ((IRM(0.3T)). The $S = \text{IRM}(0.3\text{T})/\text{SIRM}$ ratio is a measure of the proportion of magnetite to all magnetic iron oxides. (4) Remanent coercivity (B_{cr}) was determined using DC demagnetization of SIRM.

Geochemical data. Geochemical measurements were performed in the Geochemical Department of the Ecole des Mines, Saint Etienne, France. Heavy metal contents were obtained using 3050B USEPA method (Edgell 1988) on an Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

Results. The data set is divided in two subsets to define eastern industrial areas (16 samples) and the other part of the town (45 samples)

- The S ration (for most of the samples) is ≥ 0.9 . This result shows that the samples are dominated by ferromagnetic crystals (magnetite $\pm$ maghemite). Fig.1.
- The values for B_{cr} show that the samples are dominated by low coercivities magnetic minerals like magnetite (fig.2)
- The magnetic susceptibility variations are in close correspondence with ARM (fig.3), IRM and SIRM (fig.4) variations and indicate that the magnetic susceptibility values are mainly controlled by the input of ferromagnetic minerals.

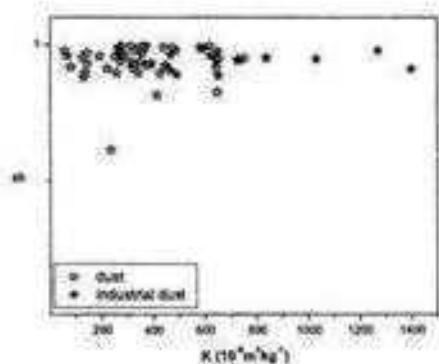


Fig.1 S – K correlation for street dust of Baia Mare

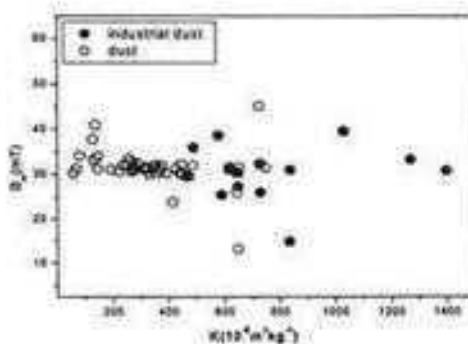


Fig.2 B_{cr} – K correlation for street dust of B.M.

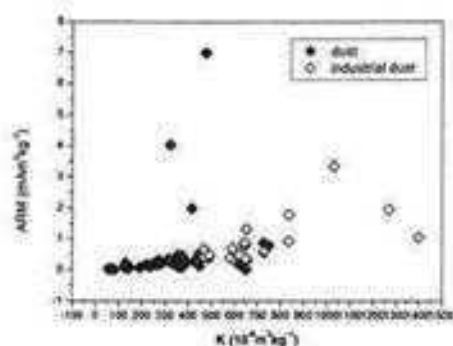


Fig.3 ARM – K correlation for street dust of B.M.

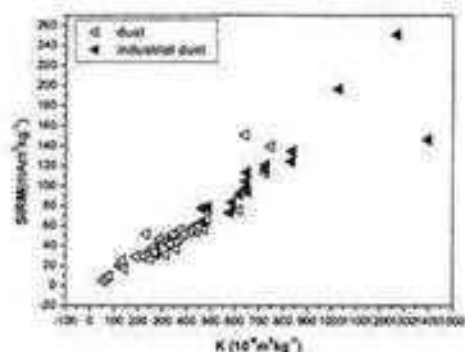


Fig.4 SIRM – K correlation for street dust of B.M.

- The average values of magnetic susceptibility are larger in the industrial area than in the rest of town. These results indicate that the magnetic susceptibility values are mainly controlled by the input of anthropogenic magnetite.
- Mean values of several parameters SIRM/K, SIRM/ K_{ARM} , K_{ARM}/K and B_{CR} compared with Peters and Dekker (2003) diagrams, suggest that most of our samples are in the range 0.03 – 10 μ m grain size variation. The trend suggests that magnetic granulometry increases toward the industrial area.
- The concentrations of heavy metals show a positive correlation with magnetic susceptibility, large values of both were found in the industrial area (fig.5, fig.6, fig.7).
- The values of the heavy metals decrease from east to west, this distribution being influenced by direction of the main air movements in Baia Mare. The trend of magnetic susceptibility is the same.
- The grain size of magnetic minerals increases in industrial area; this trend suggests anthropogenic sources and low transportation of these minerals.

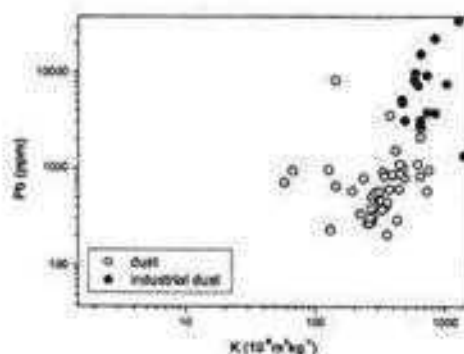


Fig.5 Pb – K correlation for street dust of B.M

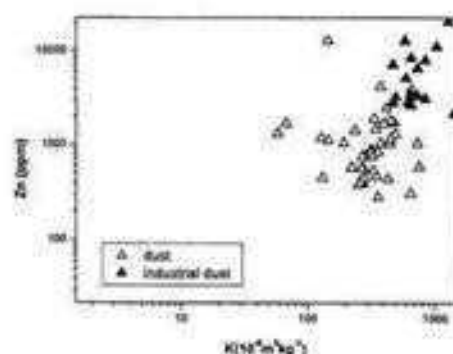


Fig.6 Zn – K correlation for street dust of B.M.

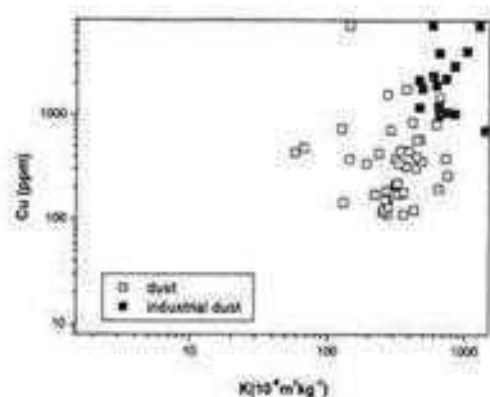


Fig.7 Cu – K correlation for street dust of B.M.

Conclusions.

- Magnetic susceptibility can be used in the Baia Mare town to map and monitor the pollution with heavy metals for street dust, but without a good selectivity for specific metals.
- Measurements of the magnetic susceptibility are not expensive and they provide a first base to map and define polluted areas.

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DISSOLVED NATURAL ACTINIDES IN RIVER WATERS AROUND A URANIUM MINE (EAST CARPATHIANS, ROMANIA)

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INTRODUCTION

Numerous authors have studied the uranium concentration in surface waters. The published data suggest very wide range of U concentrations in water, from below $0.01\text{-}\mu\text{g}\cdot\text{L}^{-1}$ to over $1,500\text{-}\mu\text{g}\cdot\text{L}^{-1}$ (0.1 to $10\text{-}\mu\text{g}\cdot\text{L}^{-1}$ in most natural waters, and over $1,500\text{-}\mu\text{g}\cdot\text{L}^{-1}$ in waters related to uranium ore deposits). These values indicate variability due to differences in the river samples, the time of sampling and sample treatment.

Compared to uranium, relatively less information was located on the levels of thorium in natural waters. The thorium content in natural fresh waters (pH 5 to 9) rarely exceeds $1\text{-}\mu\text{g}\cdot\text{L}^{-1}$. Recent results demonstrate that Th concentration in water samples from rivers is less than $15\text{-ng}\cdot\text{L}^{-1}$, in absence of dissolved organic carbon.

The study is related to uranium mineralization located within Crucea ore deposit, in the East Carpathians, Romania. In this paper we present data from four main tributaries of Bistrita River (i.e. Crucea, Troaca Gavanului, Gavan and Cracul Rau creeks) and from four sampling points on the upper course of this main stream (two points located downstream and two located upstream of the confluence with Crucea creek). The aim of this paper is to investigate the impact of mining activities on the surface water resources in the area.

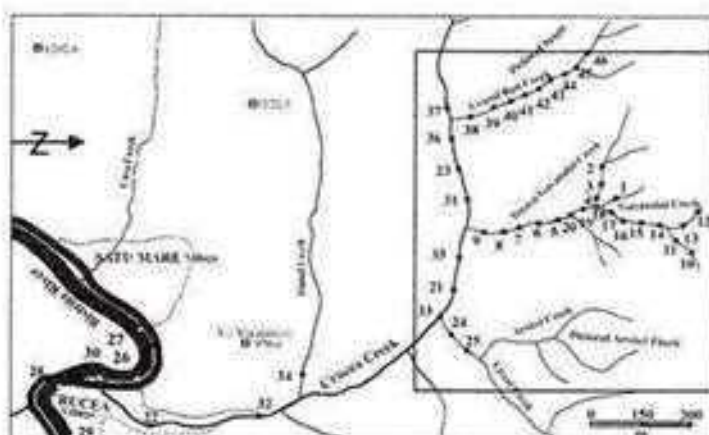
ANALYTICAL PROCEDURES

Water samples for the determination of chemical parameters, including trace metal concentrations were collected in July 2004 (season chosen for its relatively dry character, with average rainfall of 100-120 mm/month) from different surface waters in the Crucea uranium deposit and adjacent zones (The East Carpathians). Samples were collected at each sampling point from the river surface (at approximately 20 centimeters depth). The sampling location and topography of the study area are shown in *Fig. 1*.

The pH was measured in situ during sampling (one measurement per sample) using a 330 WTW pH-meter with Sentix 41 platinum electrode. The pH electrode was calibrated on site with pH buffers of 4.01 and 7.00 to bracket the sample pH value and was equilibrated to the sample temperature.

Two water samples were collected in clean 500-mL HDPE wide mouth bottles at each sampling point, one for the determination of dissolved cations and another one for anion analysis.

Fig. 1. Topographic map of the investigated area with the sampling points.



Both samples were filtered on site using a hand-pump Nalgene® through 0.45- μm , nitro-cellulose filters (Sartorius®). Immediately after collection, one of the samples was treated with 2 mL of concentrated nitric acid (HNO_3) to prevent adsorption onto the walls of the recipients.

In the laboratory, filtered, acidified water samples were used to determine the concentrations of dissolved cations.

The dissolved uranium in the water samples was determined using a pre-concentration procedure outlined by Tsutomu *et al.* (2000). The solution was analyzed for U by Inductively Coupled Plasma – Optic Emission Spectroscopy (ICP-OES), using a HORIBA Jobin Yvon ICP-OES system.

Before uranium analysis of water samples, 100-mL sub-samples of acidified water were analysed for the following elements: Si, Al, Fe, Mg, Ca, Na, K and Th using EPA Method 3005 followed by ICP-OES analysis (EPA Method 6010).

The concentrations of common anions (carbonate, sulfate, nitrate and chloride) were determined in filtered un-acidified water samples by Ion-Chromatography (IC) using a Dionex DX-600 system. In the laboratory, the water was kept cold prior to analysis.

A rigorous quality control program was implemented, included analytical-reagent calibration solutions, duplicate samples and double deionised water (MILLI-Q system, conductivity < 18 $\text{M}\Omega\text{cm}$). The degree of determinative uncertainty (2σ error) is of 5–15% for anions and 5% for ICP-OES varying with the concentration and the analysed element.

RESULTS AND DISCUSSION

Concentrations of dissolved uranium in the surface waters collected from Crucea zone can reach very significant values (up to $1 \text{ mg}\cdot\text{L}^{-1}$), thus qualifying it as the first trace element at some places. The uranium concentration ranged from a value of $0.016 \text{ mg}\cdot\text{L}^{-1}$ to $1.43 \text{ mg}\cdot\text{L}^{-1}$

¹, with a mean of $0.365 \text{ mg}\cdot\text{L}^{-1}$ (Fig.2). According to the Romanian legislation, the maximum allowed level (MCL) of uranium contamination is of $0.021 \text{ mg}\cdot\text{L}^{-1}$ of water. The uranium concentrations upstream the uranium mine are small compared with the one downstream the mining area. Waters with levels of uranium in excess of the MCL are present in the vicinity of the mine wastes. At 1,000 metres distance from the mining area, the U concentration decreases below the permissible level as a result of the dilution and adsorption in sediments and vegetation.

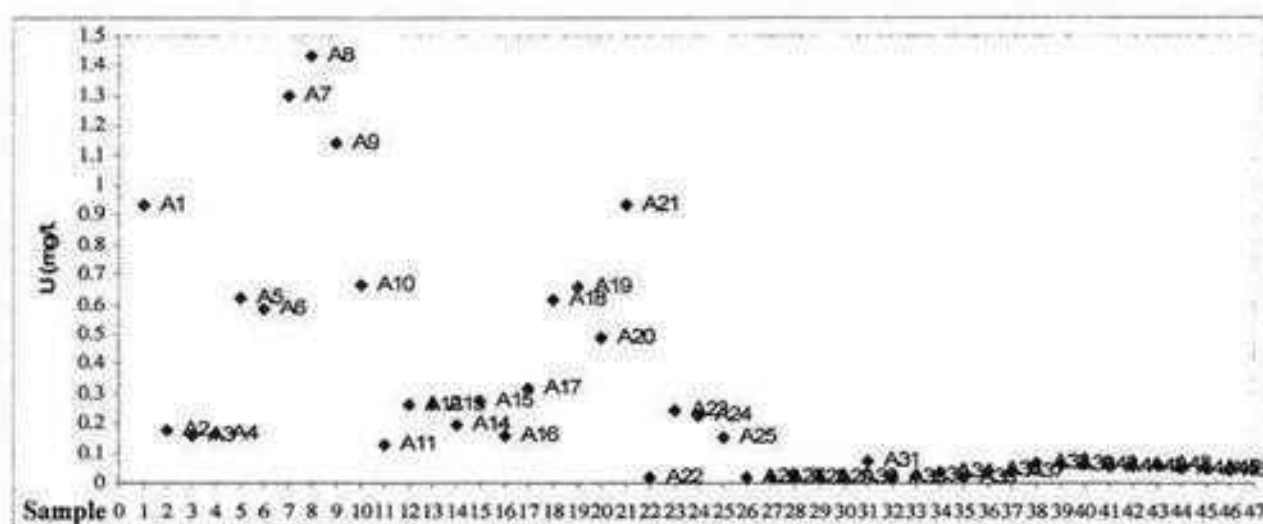


Fig.2. The uranium concentration ($\text{mg}\cdot\text{L}^{-1}$) in water samples from the investigated area. The influence of the uranium mine is distinct in this figure.

In order to investigate the factors controlling the geochemistry of uranium within the local surface waters, a correlation analysis was used. Correlation analyses between the amount of uranium in the water and the pH of the water samples show a significant dependence (Fig.3), suggesting that in a slightly alkaline environment there is an intense transfer of uranium in water.

The remarkably good correlation ($r = 0.80$) between U and total anion concentrations ($\text{NO}_3^{2-} + \text{CO}_3^{2-} + \text{SO}_4^{2-} + \text{Cl}^-$) (Fig.4) and the lack of correlation ($r = 0.47$) between U and silica (Fig.5), indicate that uranium concentrations in local water are derived mainly from oxidation of uraniferous bitumen and/or dissolution of carbonates. Based on the correlation dependence ($r = 0.69$) between U and the sum of $\text{Ca} + \text{Mg} + \text{K} + \text{Na}$ major cations (Fig.6), we find silicate weathering as an additional source of soluble uranium.

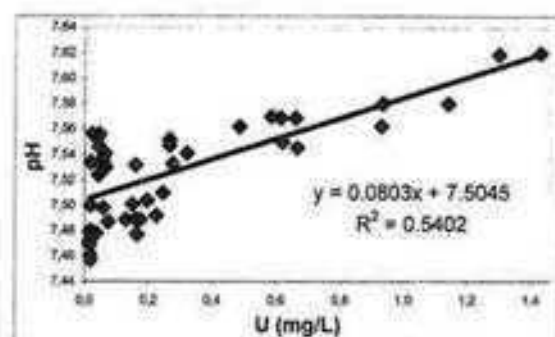


Fig.3. Variation of dissolved uranium with pH in surface waters from Crucea area (Pearson correlation coefficient $r = 0.74$).

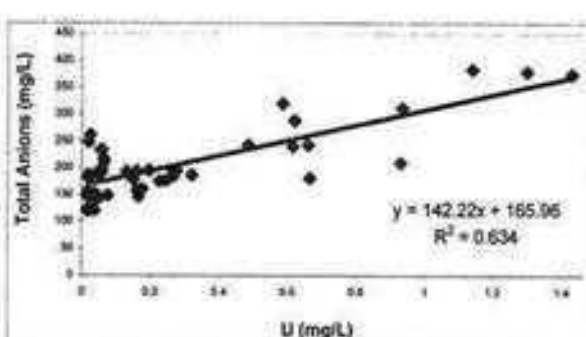


Fig.4. Variation of uranium with total anions in surface waters from Crucea area ($r = 0.80$).

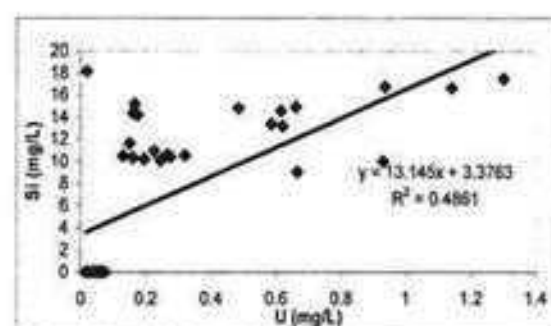


Fig.5. Variation of uranium with silica in surface waters from Crucea area ($r = 0.47$).

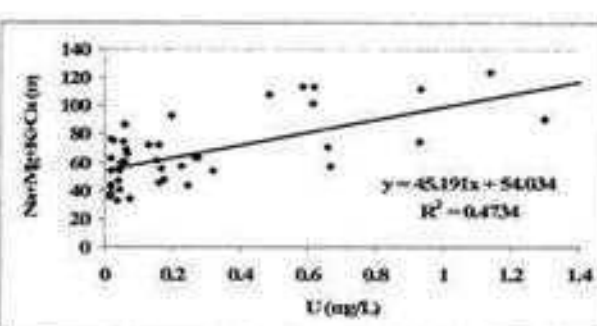


Fig.6. Variation of uranium with Ca+ Mg+ K+Na surface waters from Crucea area ($r = 0.69$).

Levels of others minor and major elements correlated well with the level of uranium concentration. For example, good correlations occur between the following pairs of elements: U – Al. The correlation ($r = 0.64$) between U and Al_2O_3 suggest that uranium could be adsorbed on the surface of clay minerals (Fig.7).

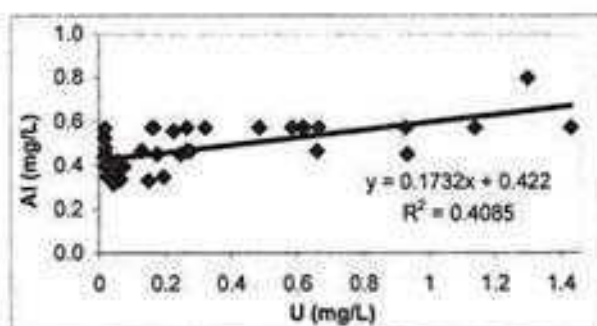


Fig.7. Variation of uranium with aluminium in surface waters from Crucea area ($r = 0.64$). It is assumed that Al concentration is proportional with the quantity of clay minerals.

Concentrations of dissolved thorium are quite low, with median values of $0.015 \text{ mg}\cdot\text{L}^{-1}$. In 76% of the water samples thorium concentrations are below the detection limit, due to the lower solubility of this element in water, as compared to uranium. In fact, these values illustrate the great chemical stability of Th and the strong tendency for dissolved forms to be adsorbed by clays, oxides and organic matter, in comparison with the significantly higher soluble (and hence mobile) uranium (which may occur both in +4 and +6 oxidation states).

CONCLUSIONS

The knowledge of uranium concentration in river waters is essential for predicting uranium migration and for the strategies concerning the rehabilitation of contaminated sites.

The concentration of total dissolved uranium in the surface waters from Crucea zone ranges between $0.016 \text{ mg}\cdot\text{L}^{-1}$ to $1.43 \text{ mg}\cdot\text{L}^{-1}$. The concentration of thorium is much lower, a mere $0.017 \text{ mg}\cdot\text{L}^{-1}$. The measurements in the surroundings of the uranium mine show that uranium concentrations in the waters of Bistrita River do not exceed the MCL.

The greatest risk posed to the environment in uranium mining area, is represented by contamination of river systems and ground water with dissolved radioactive materials. In such cases, rivers can be completely compromised as a source of water for humans and animals. The dissolved uranium in the surface waters from Crucea area comes from two sources: (1) from leaching out of waste material and (2) from weathering of silicate rocks within the uranium ore deposit.

ACKNOWLEDGEMENTS

The inorganic chemical components were determined at Département Géochimie et Procédés de l'Environnement of the Ecole Nationale Supérieure des Mines, Saint Etienne (France). The authors thank Dr. Jacques Moutte and Frederic Gallice for technical assistance.

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THE TRANSFORMATION OF SOILS PHYSICAL FEATURES FROM OLTENIA MINING SITE AFTER ECONOMICAL REHABILITATION

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1. Aspects regarding modified soils after coal exploitation

The soil suffers a great deal of damage after open coal pit exploitation (hushing, transportation, dumping) and changes of both physical and chemical properties. The resulting soil is a mixture of sand, clay and marl.

The two sections of analyzed soil (0 – 100 cm) reveal the following features: uncompacted soil, heterogeneous structure and homogenous distribution of CaCO_3 .

2. Research made emphasizes the soil physical features after mineral and organical fertilization

To emphasize the dumped soil's physical features compared to optimal values, an experiment was made between 2001 – 2004, at Cicani mining site to reveal the changes that occurred after mineral and organical fertilization and agriculture growth.

The experiment made includes mainly two aspects:

A - Species to be cultivated (a_1 – none, a_2 – potatoes, a_3 – corn, a_4 – oat)

B - Soil's fertilization level (b_1 – unfertilized, b_2 – $\text{N}_{100}\text{P}_{100}\text{K}_{100}$, b_3 – $\text{N}_{200}\text{P}_{200}\text{K}_{200}$, b_4 – $\text{N}_{300}\text{P}_{300}\text{K}_{300}$, b_5 – 40 t/ha manure, b_6 – 20 t/ha manure + $\text{N}_{200}\text{P}_{200}\text{K}_{200}$)

Only properties that can not be agrochemically enhanced were considered: texture and mineral composition.

Differences between samples were observed since the sampling.

Because the atle and the soil were improperly mixed, the resulting area has different coloured stripes.

The soils aggregate grading is the main feature of soils solid part, which plays a critical part in soil evolution. The soil's aggregate grading is unchanged, therefore the enhancing technologies must adapt to each soils texture type.

Table 1. Physical and hydrophysical features of soil from Cicani mining site, at the beginning of the experiment (2001)

Plant species	Profile	Layer	Depth	Granulometric analysis					Hygroscopicity	Texture
				Harsh sand	Hay sand	Dust	Physical clay	Colloidal clay		
None	1	A ₀	0-14	5,2	50,2	25,9	41,6	18,7	5,0	LN-LNA
	1	D ₁	14-51	0,2	63,6	15,2	32,1	21,0	4,6	LN-LNA
	1	D ₂	51-100	10,4	42,9	23,1	35,8	23,6	5,5	L
	2	A ₀	0-11	3,4	56,8	19,4	31,8	20,4	4,6	LN-LNA
	2	D ₁	11-58	1,3	63,1	19,6	24,4	16,0	4,0	LN
	2	D ₂	58-100	4,3	60,8	14,6	25,2	20,3	4,0	LN
Potatoes	3	A ₀	0-16	2,7	60,2	18,1	32,0	19,0	4,4	LN-LNA
	3	D ₁	16-33	2,0	50,0	20,6	32,7	27,4	4,3	L
	3	D ₂	33-51	2,2	70,3	6,5	21,7	21,0	2,8	LNA
	3	D ₃	51-63	8,7	61,7	13,5	30,7	21,1	4,7	LNA
	3	D ₄	63-86	6,5	54,9	15,2	29,1	23,4	4,4	LN-LNA
	3	D ₅	86-100	3,5	55,8	14,6	32,3	26,1	4,6	L
	4	A ₀	0-22	6,9	68,5	9,7	20,2	14,9	3,4	LN
	4	D ₁	22-62	4,0	88,8	2,8	7,9	4,4	1,4	N
	4	D ₂	62-100	20,3	70,9	2,1	7,2	6,7	1,6	N-NL
Corn	5	A ₀	0-20	1,0	52,9	22,0	33,4	24,1	5,0	L
	5	D ₁	20-43	1,0	55,4	17,4	36,3	26,2	5,3	L
	5	D ₂	43-96	0,4	59,6	54,6	18,2	36,2	4,6	L
	5	D ₃	96-100	36,0	48,4	1,8	17,2	13,8	1,0	LN
	6	A ₀	0-24	2,3	48,0	26,7	41,4	23,0	4,7	L
	6	D ₁	24-51	0,3	51,7	23,7	36,6	24,3	5,2	L
	6	D ₂	51-86	1,2	58,0	18,8	26,2	22,0	3,9	LN
	6	D ₃	86-100	0,3	51,2	23,4	39,7	25,1	5,8	L
Oat	7	A ₀	0-23	3,4	65,8	9,8	29,4	21,0	3,5	LN
	7	D ₁	23-60	1,6	77,6	10,6	18,3	10,2	2,2	LN
	7	D ₂	60-100	0,5	44,2	21,4	43,4	33,9	5,5	L
	8	A ₀	0-24	1,3	56,4	15,7	40,2	26,6	5,3	L
	8	D ₁	24-42	1,3	57,2	13,4	34,9	28,1	5,8	LNA
	8	D ₂	42-72	1,4	56,3	17,3	35,6	25,0	5,2	L

Table 2. Physical and hydrophysical features of soil from Cicani mining site, at the end of the experiment (2004)

Nr.crt.	Plant	Profile no.	Depth	Hydraulic conductive mm/h	Apparent density of the saturated solution g/cm ³	Apparent density of the dried solution g/cm ³	Apparent density at the reaping humidity g/m ³	Specific weight g/cm ³	Total porosity %	Humidity equivalent %	Coefficient de oillire %	Field capacity %	Ventilation porosity %	reaping bundity %	Penetration kg/cm ²
1	Not cultivated			3,62	1,48	1,48	1,53		43			19,60	13	9,07	79,8
2		P1	14- 51	1,212	1,47	1,47	1,5075	2,68	44	12,55	6,9	19,905	14	10,08	85,98
3			51- 100	0,4706	1,53	1,56	1,56	2,65	42	15,01	8,25	19,28	12	10,00	92,15
4		P2	11- 58	1,99	1,47	1,47	1,52	2,72	45	10,92	6,0	19,60	15	8,42	90,3
5			58- 100	0,4103	1,51	1,53	1,56	2,68	42	10,92	6,0	19,20	12	9,60	100,86
6	Potatoes	P3	16- 33	0,7481	1,47	1,47	1,48	2,68	46	11,73	6,45	20,00	15,0	9,31	66,3
7			33- 51	3,982	1,50	1,50	1,50	2,74	45	7,64	4,2	20,0	15	8,26	72,2
8		P4	0-22	6,905	1,35	1,35	1,35	2,71	50	9,28	5,1	22,0	20	9,85	39,9
9			22- 62	67,694	1,38	1,38	1,78	2,71	50	3,82	2,1	22,0	19	5,35	17,1
10	Corn	P5	0-20	0,6335	1,12	1,51	1,505	2,67	44	13,65	7,5	19,99	14,29	16,06	116,38
11			20- 43	6,395	1,44	1,42	1,45	2,71	47	14,5	7,9	20,48	16,0	45,27	93,1
12		P6	0-24	0,6589	1,48	1,42	1,50	2,67	45	12,83	7,05	20,33	15	13,32	86,4
13			24- 51	2,706	1,42	1,42	1,42	2,68	47	14,19	73,8	21,05	18	12,43	60,8
14			51- 86	10,237	1,33	1,39	1,39	2,68	51	10,64	5,85	22,79	21,33	11,96	28,5
15	Oat	P7	0-23	21,650	1,246	1,24	1,25	2,66	52	9,55	5,2	24,13	23	10,09	22,8
16			23- 60	24,181	1,50	1,52	1,55	2,68	43	6,0	3,3	19,36	13	11,70	71,3

3. Results and discussions

Physical analyses were made at the beginning (2001) and at the ending (2004) of the experiment:

a) at the beginning of the experiment the following facts were acknowledged:

- the researched soils had a sandy loam and loamy-sandy-clay texture
- the colloidal clay content was 4,4 to 36,2% (frequently 20 – 24%)
- the clay content varies between 7,2% and 43,4%, frequent values of 25-30%
- the other components had different values (depending on depth and profile) harsh sand – 0,2 – 36%, hay sand 42,9% - 88,8%, dust 1,8 – 54,6%

b) at the end of the experiment (2004) the results were:

- the aggregates grading variations is influenced by the bad mixing of soil with attle and not by plant species;
- the apparent density had values between $1,16 \text{ g/cm}^3$ – $1,56 \text{ g/cm}^3$
- the specific weight had values between $2,66$ – $2,71 \text{ g/cm}^3$
- values for the ventilation porosity were ranging between 11% and 30%
- the penetration opposition shows the heterogeneity of dumped materials - the values are: $9,2 \text{ kg/cm}^2$ – 140 kg/cm^2 .

4. Conclusions

The physical and hydrophysical features of analyzed soil does not respect the properties of an evolved, typical soil, but it shows very different properties by profile, layer and areas, the determineted factor being the nature of the native excavated, transported and randomly dumped soil.

ALGAL BIOTEST APPLICATION, FOR TOXICITY ASSESSMENT OF POLLUTED SEDIMENT IN OLT RIVER AREA.

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This study attempts to offer a short description of the effects of water pollution and of some preliminary data regarding the toxicity of suspended and bottom sediments. Also, this study brings into focus the changes which evolve in aquatic systems inputs yield because of the human activities. The aquatic environmental quality especially depends on the direct introduction of industrial waste and pollutants into water.

In this case the assessment of water & sediment quality is made with *Selenastrum capricornutum* Printz biotest, on some sampling from Olt River. The unicellular green alga *Selenastrum capricornutum* Printz growth inhibition biotest is applied for determining the presence of toxic substances in environment. The U.S. - Environmental Protection Agency 600/9-78-018, July 1978 standard protocol was followed, and growth rate inhibition were determined by direct counting of *Selenastrum capricornutum* cells. This biotest represent a reliable and readily usable micro-plate technique method.

The quality of water becomes worst because of the physical, chemical and microbiological modifications. The main reason for water quality decrease is represented by: residual industrial waters, sewages, fertilizations, waste products, etc. If water presents a high degree of contamination, then polluted water becomes inadequate to maintain the aquatic life reducing also the capacity of reproduction and finally has after-effects on human health.

Chemical substances represent the main provoking agent for water and sediment contamination. Sample toxicity detection (water/suspended solids/bottom sediment) may be efficiently investigated by algal toxicity bioassay with *Selenastrum capricornutum* Printz algae. Because of the microorganism sensitiveness to water quality changes, these algae can be used as a pollution indicator. Usually the algae growth in favorable physical-chemical conditions (temperature, light, dissolved oxygen, mineral salts, etc.). Algae can have an influence upon water composition too, and in certain limits can assimilate some chemical substances supplied by wastewaters.

The main problems which affect environment in the Ramnicu Valcea County it mainly refers to the pollution due to chemical agents from: chemical industry (caustic soda, polyvinyl

chloride, insecticides, pesticides, alcohols, and polycarbonates), processing industry, energetic and thermal industry, agricultures, etc.

This present work paper is focus on toxicity determination of water and sediment samples from Babeni & Govora reservoirs, Topolog tributary, and also for estimation bio-limitative factors (such as N & P).

Babeni (situated downstream Chemical Plant) and Govora reservoirs were mainly selected because received a lot of industrial discharges (from industry, agriculture, sewages, etc.)

Topolog affluent was chosen for comparison and because in this area there are no recognizable pollution sources.

Other points: Govora River, Focsa outlet tributary, and one effluent from Ramnicu Valcea purification station.

In sampling campaign, there have been collected water & sediment specimens (bottom and suspension sediment) from some station as: Babeni-Govora lakes, Topolog, Focsa, Govora tributaries, and also for Ramnicu Valcea purification station. Suspension sediment samples were collected with Alpha-Laval Sedisamp system centrifuge. Some physical variables were measured *in situ*: temperature, dissolved oxygen, oxygen saturation, conductivity, total dissolved solids, pH, and salinity

The protocol used in this work paper was firstly applied in Romania by Bostan et al. (1998) and Bostan (2001) in evaluating water & sediment samples from Danube and Danube Delta. This protocol is based on the US-EPA Standard algal assay bottle test (Miller et al., 1978) and on its micro-plate adaptation, with a reduced incubation time associated with a higher initial number of algae as by Environment Canada (1992). Some versions of this test for micro-plates were described and used by Pardos et al. (1996) and Laibargt et al. (1991).

The *Selenastrum capricornutum* Printz represent a short-term method for estimating the toxicity of water and sediment. This biotest could assess the effects of chemical products or environmental samples on the growth or inhibition of the algae after a 72 hour incubation period. The presence of one compound or compound association which shows a rate of toxicity could be interpreted as algal inhibition versus control solution. Increased quantities of nutrients in analyzed sample determine an algal overloaded.

This work is focused on toxicity sediment sample from Babeni, Govora & Topolog River, and also for bio-limitative factors determination versus one control sample.

There were analyzed some suspension sediment samples from Babeni (01, 02, 03, 04 stations), Govora (05), Topolog affluent (06), Govora (07, 09) and also for Ramnicu Valcea purification station effluent. First of all it's better to mention that the majority of sample

present a disagreeable odor and extremely persistent, the elutriates from 01, 02, 03, 04 and 05 sample present a dark brown color. Because of this fact the microscope algae counting become more difficult for 02, 03 and 04 samples.

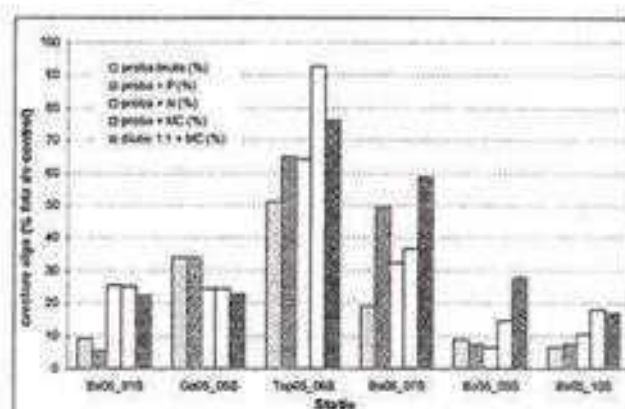


Fig.1 The algal growth in suspension sediment elutriate

The bioassays used for these samples were realized on the same micro-plate which includes 05 samples, too. In this micro-plate was observed a strong algae inhibition for all the samples, inclusively for the synthetic nutrient medium used as standard etalon. This fact suggest a strong toxicity for 02, 03, 04 samples. An explanation for this could be the toxicity of volatiles compounds which throw re-dissolving processes, can contaminate the majority of samples.

For the majority of samples it can be distinguished an inhibition for the algal growth versus control (synthetic nutrient medium). This fact indicates a strong toxicity for all analyzed suspension sediments. We have to mention that the strong toxicity for 05 case samples - Govora lake could be influenced by sample from Babeni lake, because all the sample were analyzed simultaneously on the same micro-plate. Evidently toxicity for 09 sample collected from Govora tributary, near Govora lake outlet, emphasizes the strong toxicity for 05 sample gathered from lake.

The sample collected from Topolog affluent (06) is also characterized by an inhibition on the algal growth versus control (synthetic nutrient medium), but we can say that it seemed to be more "clean" comparatively with the other one samples.

We can not appreciate the toxicity for the entire bottom sediment samples because of the fact that the majority of bottom sediment samples were not yet analyzed. The analyzed bottom sediment samples 01, 02 and 02 from A strata (02BsA) present a light toxicity versus suspension sediment samples.

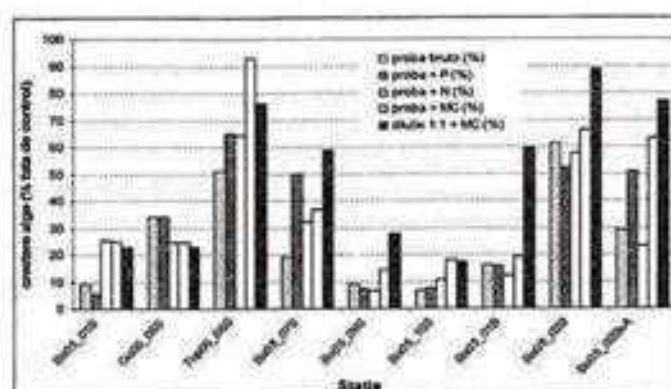


Fig. 2 The algal growth for all analyzed samples

In this case we can observe a strong toxicity for the majority of samples. This indicates an obvious toxicity for the chemical compounds present in sediments, but we can emphasize that the bottom sediment are less toxic than the rest of the sample.

To base on acquired data as a result of bio-test performing we can made a preliminary aquatic environment quality characterization for our case study.

The acquired results show that this biotest was very helpful in predicting toxicity. The majority of samples present potential toxicity. This fact could indicate the presence of toxic substances in sediments, or another variant could be the incomplete degradation of some products present into the studied sample.

It is better to mention that for a rigorous interpretation it is necessary to combine all types of analyses. Also, one species is not sufficient to present a total response for the entire biological community and for the whole aquatic system.

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ACTUALISTIC NUMERICAL SIMULATION OF IMPACTED GROUNDWATER FLOW ORIGINATING FROM A DECOMMISSIONED TAR MANUFACTURING PLANT

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1. INTRODUCTION

Numerical simulation of fluid flow and solute transport in the case of landfill spills represents a versatile tool when assessing the extent of pollution and remediation strategies (Fatta et al., 2000). The paper describes the hydrogeological simulation, by using finite elements, of the contaminant plume migration at a tar manufacturing plant, situated in the floodplain of the Main River. The current mass distribution of the contaminant plume represents a result of the historical spills and leaching of substances from the on-Site fill materials. The hydrogeological modeling achieved the current conditions, followed by characterization and delineation of the impacted riverbank groundwater given several remediation alternatives.

2. GEOLOGICAL SETTING AND HYDROSTRATIGRAPHIC UNITS

The overburden deposits are formed by glaciolacustrine clay and silty clay. The glaciolacustrine deposits are subdivided into three units, from top to base: brown, weathered clay, gray, unweathered clay and silty deposits (Figure 1). There are three groundwater – bearing units on the Site: the upper brown clay/fill complex, the glacial till/lower lacustrine complex and the bedrock. The correspondence between the stratigraphic and hydrostratigraphic units: upper brown clay/fill complex and glacial till/lower lacustrine complex represent the shallow aquifer, while bedrock is the aquitard.

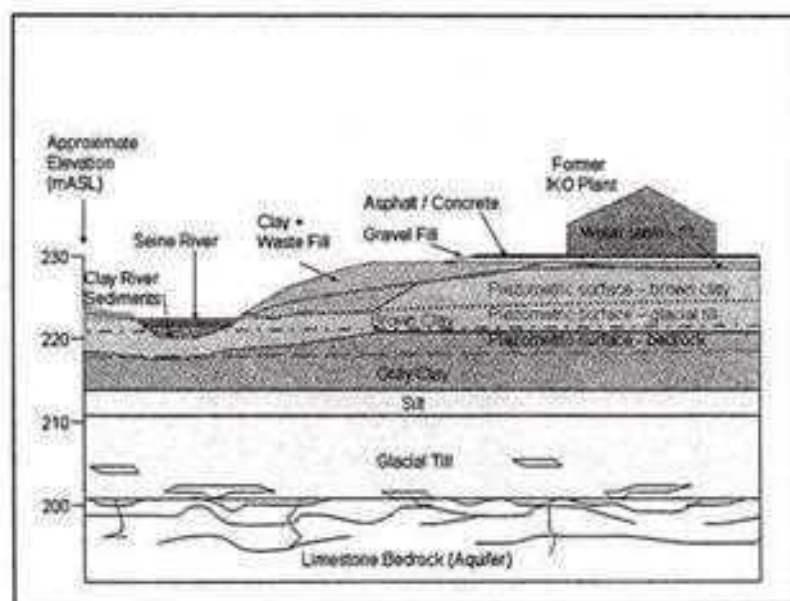


Figure 1.
Generalized stratigraphy

3. CONCEPTUAL HYDROGEOLOGICAL MODEL

The conceptual hydrogeological model represents the basis for the construction of the numerical hydrogeological model (Figure 2).

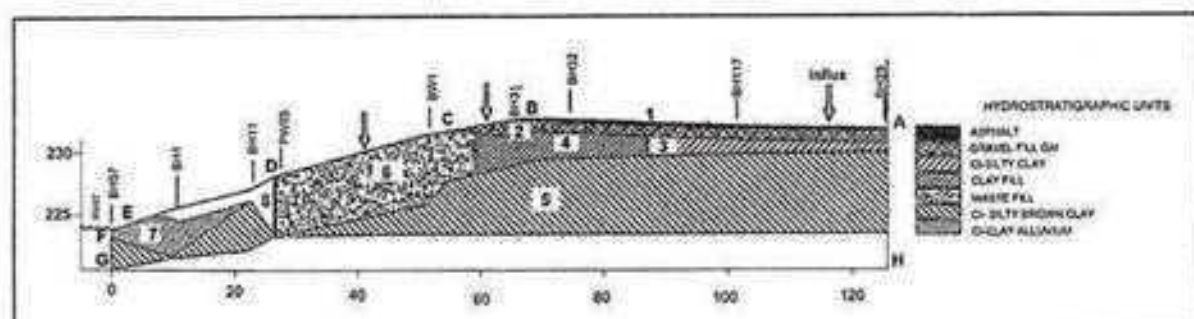


Figure 2 Conceptual hydrogeological model

The units of the hydrostratigraphic conceptual model are as follow (where K denotes hydraulic conductivity at 10^{-4} m/s and ϕ percent porosity) : 1-new asphalt, $K=0.0001$, $\phi=10$; 2-gravel fill, $K=0.125$, $\phi=30$; 3- silty clay (grey black clay), $K=0.0014$, $\phi=25$; 4- clay fill, $K=0.014$, $\phi=25$; 5- CI-Silty clay (brown clay), $K=0.0042$, $\phi=20$; 6- Waste fill, $K=1.36$, $\phi=30$; 7- CI-Clay (alluvium), $K=0.0014$, $\phi=20$; 8- backfilling of waste, $K=1.36$, $\phi=20$.

3.1. BOUNDARY CONDITIONS

The fluid flow boundaries for the Shallow aquifer were assigned as (Fig. 2): AH and HG impermeable to fluid flow; FG permeable to fluid flow; AE, constant recharge rate from precipitation, with a flux of 513mm/year; FE a head-dependent flux condition. Benzene and naphthalene were selected as indicator parameters of pollution. For naphthalene, the steady state simulations revealed concentrations at the river boundary below the standard criteria for fresh water, implying no further cleaning action. For benzene, with a fresh water standard criterion of 370 $\mu\text{g/l}$, the maximum detected concentration was of 11,800 $\mu\text{g/l}$. As a result, the simulations were performed to assess the effect of remedial strategies for benzene distribution on the river bank. The mass boundaries for benzene were assigned as (Fig. 2): no mass boundary conditions for AH, FG and HG; a constant mass condition from A to the end of the contaminated area, depending on the various scenarios. Where the contaminant waste has been removed, the mass input for boundary conditions is regarded as fresh water.

4. GROUNDWATER FLOW MODEL CONSTRUCTION

FEFLOW® was used to simulate the spreading of the plume. The Post Conditioned Bi-conjugate Gradient Stable Matrix method solved the groundwater flow equation. The model accounted for variable fluid density, according to extended Bousinesq approximation. The

unsaturated material was described by the Van Gentuchen - modified (α , n , m parameters) empirical law for capillary pressure and relative conductivity. The numerical stabilization was achieved by Petrov-Galerkin least square upwinding (PGLS) method.

5. PREDICTIVE SIMULATION RESULTS- EFFECTS OF VARIOUS REMEDIAL STRATEGIES

Several remedial scenarios were developed: A1- removal of 1/3 of the most impacted soil, backfilling with clean excavation spoils, AB asphalt cover; A2 - removal of 1/3 of the impacted soil, backfilling, AD asphalt cover; B1- removal of 1/2 of the impacted soil, backfilling, AB asphalt cover; B2- removal of 1/2 of the impacted soil, backfilling, AD asphalt cover. "D" location is on the surface, at the contact between the clean, backfilled/contaminated areas.

The vertical/horizontal ratio scale of the hydrogeological model has been modified for better visualization.

Figure 3 presents the actual distribution of the contamination mass. At present, contamination reaches the river and riverbank at concentrations of 400 -600 $\mu\text{g/l}$.

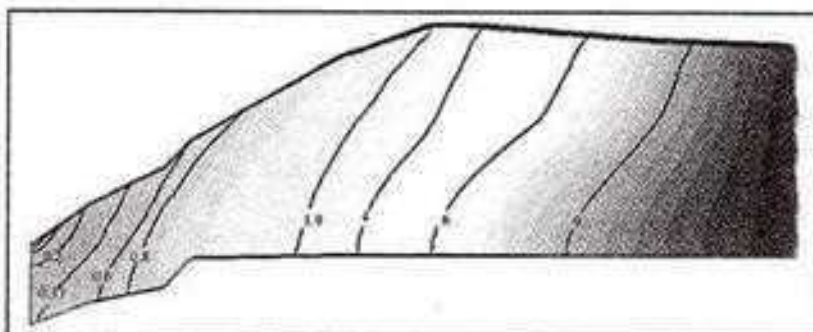


Figure 3 Actual distribution of the benzene as contaminating mass

Figures 4,5,6,7 present the remedial strategies A1, A2, B1 and B2 respectively

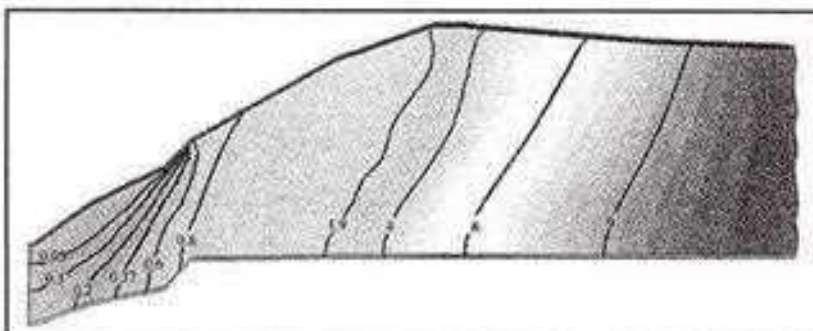


Figure 4 Distribution of the benzene as contaminating mass for alternative A1

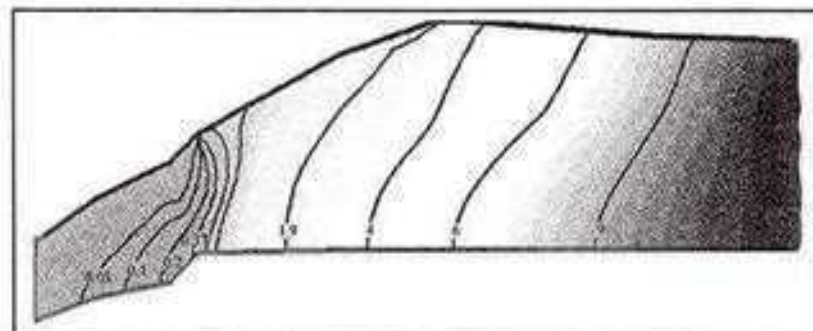


Figure 5 Distribution of the benzene as contaminating mass for alternative A2

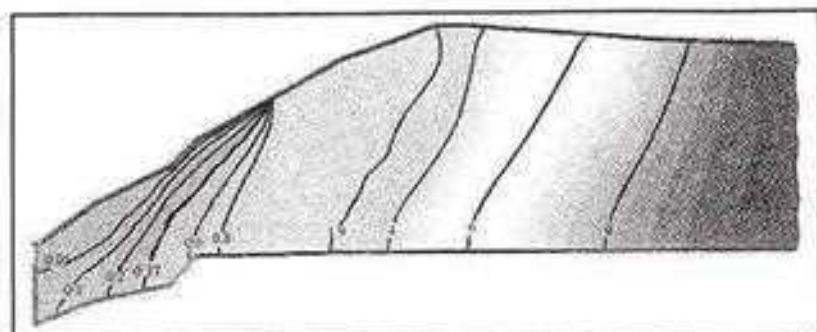


Figure 6 Distribution of the benzene as contaminating mass for alternative B1

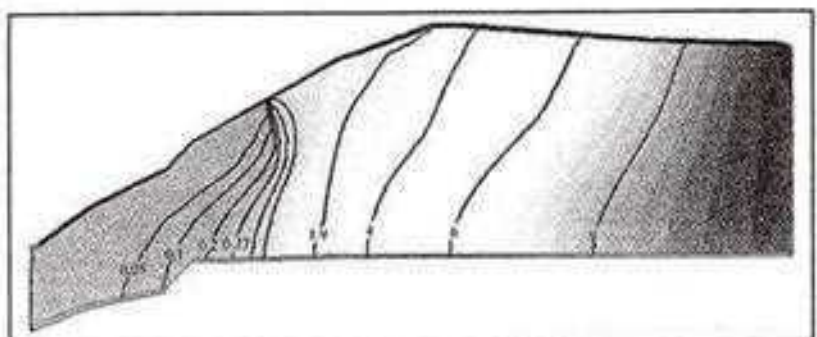


Figure 7 Distribution of the benzene as contaminating mass for alternative B2

6. DISCUSSION OF RESULTS AND CONCLUSIONS

The contour of 370 $\mu\text{g/l}$ was used as a reference comparison for the spreading of the contaminant plume in the riverbank area. As it can be observed from the pattern of the contaminant mass contours, the most important factor in the remedial action is represented by the extent of asphalt cover over the surface. Meanwhile the excavation of one third versus the half of the waste, followed by backfilling of the excavated volume with clean material, at the same hydraulic parameters, does not create very significant difference in the distribution of the contaminant, the extended asphalt cover over the whole impacted surface reduces considerably the pollution. Given the precipitation rate which remains constant as an influx, the presence of the highly impermeable asphalt cover diverts the run-off water over the clean area. As a result, the fluid flow is increased and accordingly the mass transport in the cleaned area. It is important to keep the same hydraulic parameters for the backfilling, at high hydraulic conductivity and porosity. More impermeable backfilling material allows only a reduced groundwater flow in the clean area and, consequently, the fluid flow is diverted underneath, flushing away towards the river the contaminants from the impacted section of the model.

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MAJOR ELEMENTS VARIATIONS IN SOILS IN THE SLANIC PRAHOVA SALT MASSIF AREA

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An environmental region evaluation cannot be done without taking into account the state of soils, because a damage of soils state can generate severe health problems for human being communities and as well as for animals.

It is known that the features of waters and lithological context from a zone can influence the quality of soils. Any soil, through its nature can kept some polluted elements, or can missed others, due to the circulation and chemical content of waters or the lithological features of the solid support, which support or help to form it.

So, a detailed study of the upper part of soils, about 30 cm depth, where the majority of plants have their roots and extract the necessary food, is necessary, especially in those zones where there are/were anthropic activities, respectively industrial or mining ones.

Such a study has been done in the Slanic Prahova salt massif area, where the mining activities have a long history and are still in development.

Soil samples have been collected from entire area and limitroph of the salt massif (Fig. 1), so that they are representative for different type of soils; the samples are closely located to natural and anthropic sources (salt or mineralized spring, rich gypsum rocks, closely to salt exploitation points).

The samples have been chemical investigated for major elements are presented in Tab. 1.

The variations of the major elements have emphasized specific characteristics for each soil type, higher concentrations for the majority of major elements in vicinity of salt springs, an increasing of the Na, Mg, Al contents closely to the salt springs and random distribution for others.

The major elements area distribution (Fig.2) is specific for each element, as follows:

Na₂O area distribution emphasized its concentration in the Eastern part of the investigated area, where there is defined a maximum zone; it is obviously a values decreasing to North, East and South, where the lowest values are registered.

K₂O presents no specific concentrations, outlined by the area distribution, when some maximum and minimum zones are defined in entire investigated area; the lower values belongs to collected soils from the central part of the Slanic Prahova salt massif and the higher ones are met in East and West zones.

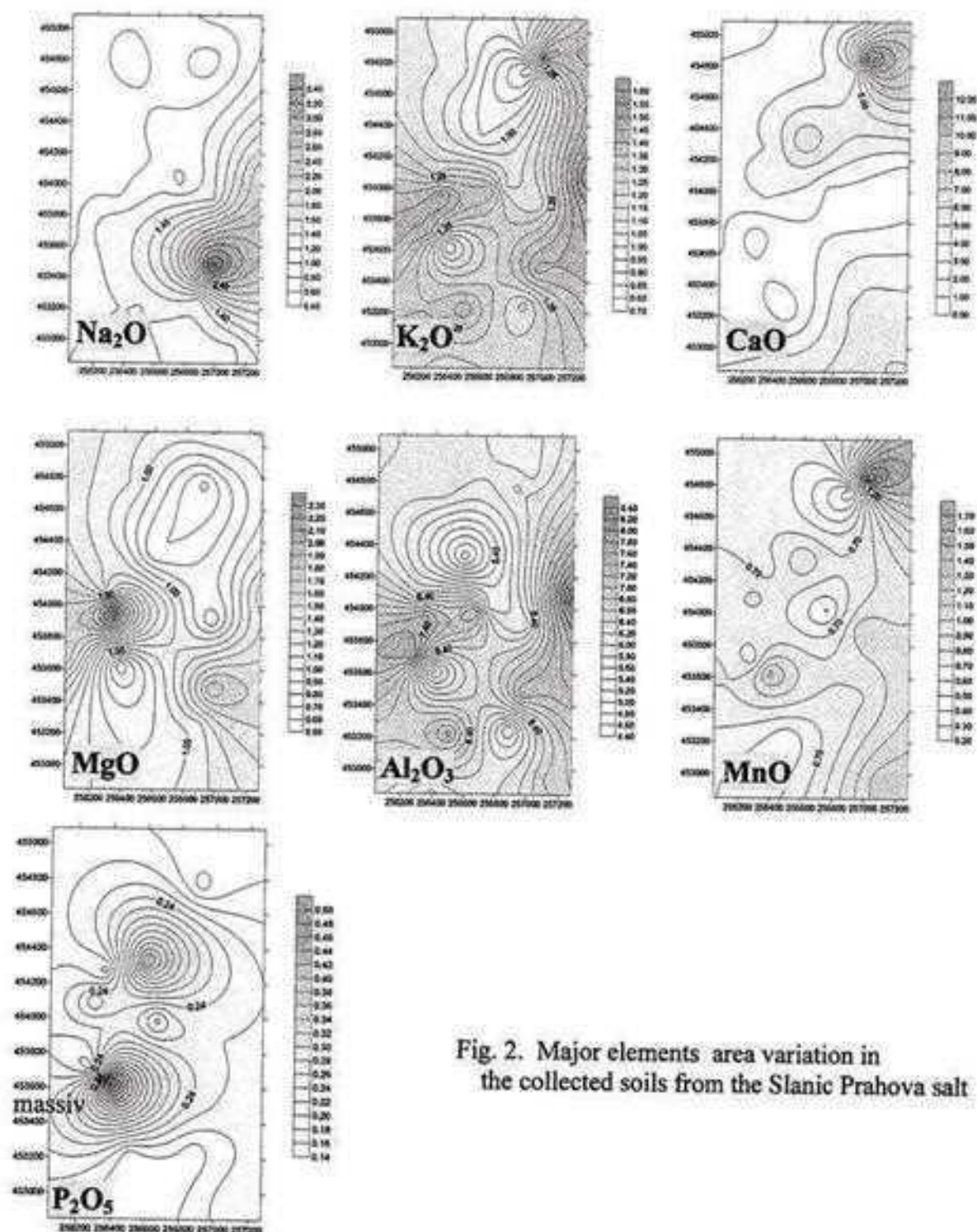


Fig. 2. Major elements area variation in the collected soils from the Slanic Prahova salt

CaO area distribution emphasizes a cross cutting minimum zone in the central part of the Slanic Prahova salt massif, determining a division of the investigated area in two compartments, the North one, where an extended maximum zone is well defined and a South one, where the CaO values register a slowly increasing.

MgO tends to concentrate in the Eastern and Western parts of the Slanic Prahova salt massif, where the highest values were found and two obvious maximum apexes have been

defined, superposed on the setting of two salt springs; there is an extensive minimum area between these zone, with two minimum apexes, outlined by the collected soils from Piatra Verde top and Baia Rosie caught salt spring.

Al_2O_3 has the highest values, emphasizing in this way the influence of the solid background on the chemical soil composition, taking into account the lithological context (predominance of the clay minerals in the investigated zone), Al abundance in the terrestrial crust and chemical proprieties of aluminum (mobility, migration and deposition).

The Al_2O_3 area distribution emphasizes random values distribution and Al affinity for the salt springs, marked by maximum zones.

MnO has low contents, with concentration of higher values in the North-Eastern part of the salt massiv, where an obvious maximum apex occurs; the rest of values slowly decrease to South-West and North-West.

P_2O_5 emphasizes low and very similar values, outlining in this way, the absence of the rich P polluted factors; these variations are marked through defining of two important maximum apexes, set in North (Baia Rosie salt spring) and South, divided by extended minimum zones.

It is obviously a contents decreasing of the majority of major elements in the Baia Rosie salt spring zone, due to its catching and use in the therapeutic treatments.

This fact demonstrates that the catching of the salt spring can be an efficient depollution method of those zones, where there are the salt springs.

WATER DEPOLLUTION BY USING ZEOLITES

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Depollution of waters, especially the mining ones, is one of the important target for the majority of the European and non European countries.

For solving of this problem, many research institutes involved in the environmental problems try to find ways and procedures for polluted content decreasing in the different kind of waters (surface water network, phreatic and groundwater ones).

According to the European and international tendency regarding the water quality, this study had tried to find an original procedure for decreasing of the heavy metal content from the surface water network cross-cutting the mining zones, by using zeolites.

The following stages have been necessary for establishing of an original method:

- 1- the stage of the complex study of the zeolitic occurrences, when different zeolitic outcrops from the Transilvanian Basin, hosted by "Tuful de Dej", have been investigated through different methods (direct observations in the outcrops, microscopical, physical and chemical investigations), for identification of those mineral species and properties of this special minerals group, absolutely necessary for their using in the water depollution.

So, Dej-Nasaud Zone (Jichesu de Sus - fig. 1, Cepari, Dej occurrences) has been studied and some zeolite samples have been collected and analysed.

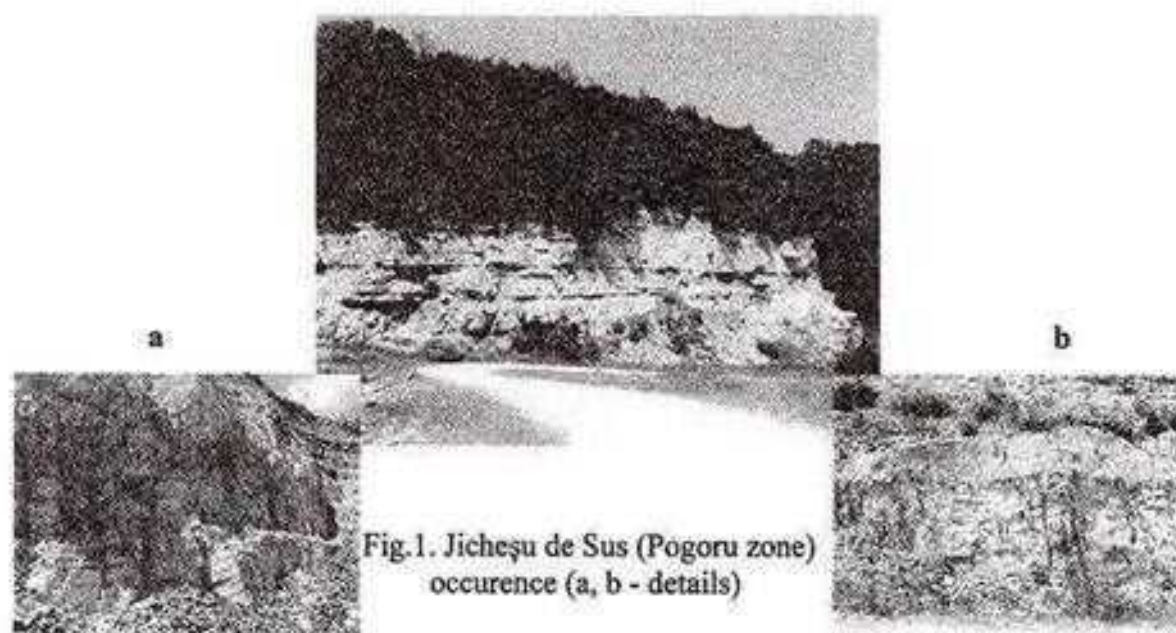


Fig.1. Jichesu de Sus (Pogoru zone)
occurrence (a, b - details)

The X-Ray diffraction investigations have emphasized different zeolitic species and mineral associations (Tab.1)

Table 1. Zeolite species and mineral associations in the Dej, Jichesu de Sus and Cepari occurrences

1	Zt9-N ₁	Dej	Ferrierite, Mordenite
2	Zt9-N ₂		Epistilbite, Ferrierite
3	Zt10-N ₁	Jichesu de Sus (Pogoru)	Epistilbite, Ferrierite, Mordenite
4	Zt10-N ₂		Epistilbite, Ferrierite, Mordenite
5	Zt11-N ₁	Jichesu de Sus (Colina Malu)	Epistilbite, Ferrierite, Mordenite
6	Zt11-N ₂		Thomsonite, Natrolite
7	Zt12-N ₁	Cepari	Scolecite, Mordenite, Faujasite
8	Zt12-N ₂		Thomsonite, Natrolite, Scolecite

Chemically, the investigated zeolites have the similar chemical compositions, related to the theoretically ones; constantly, Al, Si, Na and Ca, have been identified, but Fe^{3+} and K^+ have been frequently included, emphasizing in this way the possible substitutions between Al- Fe^{3+} and Na-K in their crystalline network.

- 2- the experimental laboratory stage, when it has been elaborated the laboratory depollution procedure of the contaminated water, through (i) the establishing of the sample preparation scheme and (ii) experimental laboratory way of water depollution, when four types of experiments have been tried (Fig. 2): column with the 10ml/min flow (B), column with the 170ml/min flow (C), 24 hours stationary (D) and 2 hours mixing (E) (Fig.2).

The mixing way has been the most efficiently one, the majority of heavy metals contents have been obviously decreased (Tab.2).

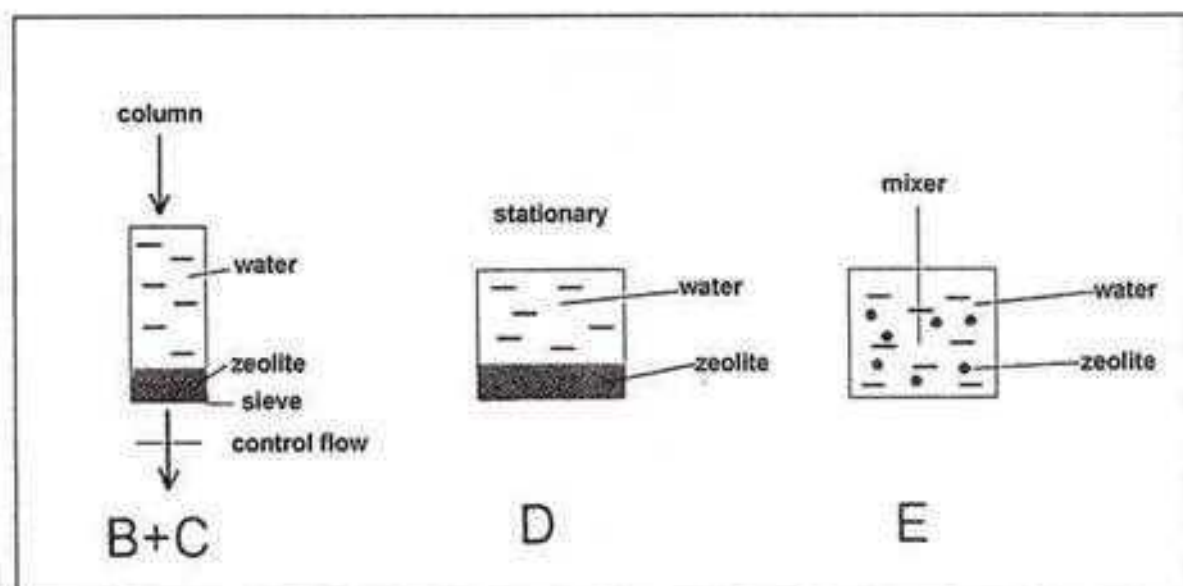


Fig. 2. Experimental laboratory ways for water depollution
*B+C = column with checked flow (10ml/min and 170ml/min);
 D=24 hours stationary; E= 2 hours mixing.*

Table 2. Variation of heavy metals contents in waters before and after zeolite using

No.	Metal	Initial heavy metal concentration mg/l	Heavy metals concentration after zeolite using (Pogoru) mg/l	Heavy metals concentration after zeolite using (Cepari) mg/l
1	Fe	7.855	0.139	0.249
2	Mn	24.321	14.568	17.569
3	Pb	0.230	0.102	0.102
4	Zn	14.619	3.434	8.594
5	Cu	0.837	0.127	0.464
6	As	0.097	0.015	0.041
7	Al	29.128	0.428	0.428
8	Cd	0.080	0.020	0.041
9	Co	0.193	0.126	0.137
10	Ni	0.292	0.126	0.207

- 3- The experimental field stage, when a zeolite sample collected from Jichesu de Jos (Pogoru zone) occurrence has been used for depollution of the v. Arsului brook water South Apuseni Mountains).

The mixing way has been chosen, because it mostly reduced the heavy metals contents in the laboratory stage; the water samples have been collected at the different time intervals, respectively one, two and three hours and chemically investigated.

The analytical investigations show a different but significant decreasing of the heavy metals concentrations (Tab.3).

Table 3. Variation of heavy metals contents in waters before and after zeolite using (mg/l)

No.	Metal	Initial heavy metal concentration in water mg/l	Heavy metals concentration after zeolite using (1 hour)	Heavy metals concentration after zeolite using (2 hours)	Heavy metals concentration after zeolite using (3 hours)
1	Fe	3.445	3.345	3.326	2.967
2	Mn	148.02	145.80	138.40	138.20
3	Pb	0.030	0.030	0.028	0.028
4	Zn	28.21	27.83	27.56	26.65
5	Cu	139.0	138.1	128.4	120.5
6	As	0.01	0.089	0.084	0.081
7	Mo	0.001	0.0007	0.0006	0.0006
8	Cd	0.486	0.486	0.472	0.448
9	Co	1.802	1.786	1.649	1.625
10	Ni	0.334	0.334	0.310	0.296

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NATURAL AND ARTIFICIAL ACID MINE DRAINAGE PRODUCTS

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The present paper deals with a mineralogical and a geochemical characterization of both natural and artificial products of the acid mine drainage (AMD). In this respect, our study focused on samples from Balan mining area: AMD products (secondary minerals) sampled from the Wetter quarry and from the mine wastes of Balan exploitation perimeter. The rock debris on which the secondary minerals occur are represented by low-grade metamorphic rocks (Tulghes Group) with traces of sulfides (mostly pyrite and chalcopyrite).

The AMD products occur on rock debris from the slopes of Wetter quarry; they look like efflorescence of green-yellowish to yellow-brownish color occurring on rock debris with traces of pyrite and like efflorescence of greenish to bluish color in the case of debris with traces of chalcopyrite. Secondary mineral formations have been found especially on northward oriented faces of rocks debris that protect it against the exposure to the sunlight and to the drying processes which would cause their dehydration and disintegration.

Natural AMD products (secondary mineral formations) from Balan perimeter consist mostly of Mg, Fe, Al hydrated sulfates; the mineralogy of some of these products has been described by Nicolaev (2006) as presented in table 1. The mineralogical terms identified using the XRD method match to the mineralogical composition published by Hammarstrom et al. (2005) for quite similar occurrences in eastern United States.

Table 1 Mineralogical composition of natural AMD products (from Nicolaev, 2006)

Sample	Mineralogical terms
220a	Alunogene, magnesiocopiapite, aluminocopiapite, romerite
222	Alunogene, pickeringite, halotrichite, romerite, kalinite
223	Alunogene, pickeringite, apjohnite, kalinite
225	Alunogene, magnesiocopiapite, pickeringite, halotrichite, jarosite, romerite, kalinite, gypsum
226	Alunogene, jarosite

The experimental studies we performed revealed a high dissolution rate of AMD products in distilled water. In this respect, the samples (of about 10g) from different occurrences have been placed on a filter paper in different funnels; afterwards, about 50ml distilled water (19°C, pH = 6.3) has been poured on each sample. The leaching has been

performed three times for each sample and the leachates have been collected in Berzelius vessels; after the third leaching, no solid sample remained on the filter paper.

The leachates generally keep the color of initial efflorescence, only that the color is far lighter initially and darkens only after the first 24 hours from the leaching process; after this period of time precipitates on the bottom of the collector vessels have been observed also. The pH of leachates has been measured using a MeterLab PHM 250 Ion Analyzer – Corning M555, showing values ranging between 1.6 and 3.5.

In order to look out on the relationship between the grain size of AMD products submitted to the leaching process and the pH of the leachates, each sample has been separated in four categories as follows: grains of more than 4mm in diameter, grains of 4-2mm, grains of 2-1,4mm and grains of less than 1,4mm in diameter. The diagram of figure 1 shows a very slight decreasing of pH, from the largest grains, towards the smallest; this rule only stands for the first leaching (sample 220a).

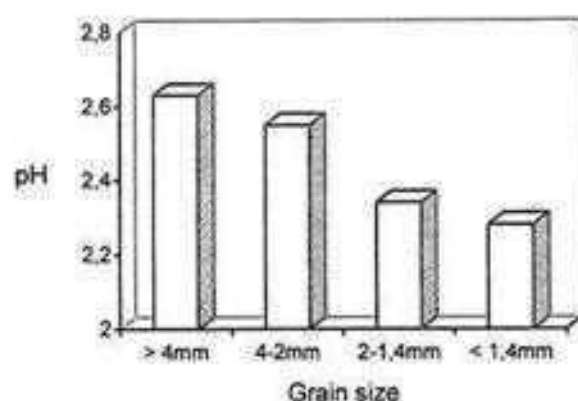


Fig. 1 pH vs. grain size (sample 220a)

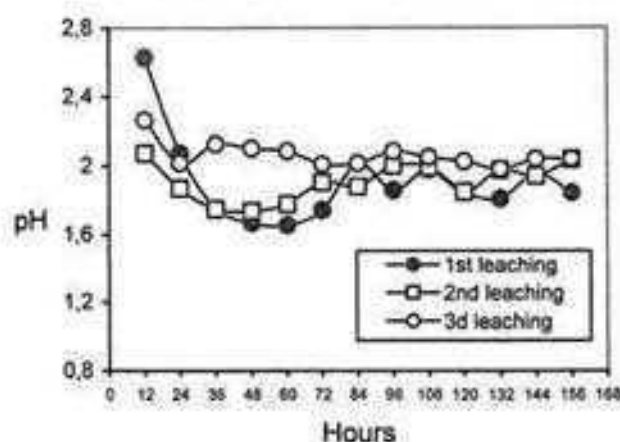


Fig. 2 pH of leachate vs. time (hours) (sample 220a)

The leachates have been kept in Berzelius vessels for about two weeks; during this time, two pH measurements by day have been performed. The variation of pH in time (fig. 2) (sample 220a) reveals for all three leaching processes a lowering of pH values in the first hours of the experiment; the diminution of pH lasts for about 60 hours (1st leaching), 48 hours (2nd leaching) and 24 hours (3^d leaching).

The lowest pH value has been recorded for solutions emerged from the first leaching process (pH ~ 1.6) and the highest pH is characteristic to solutions emerged from the third leaching process (pH ~ 2.0). After this period of time, the pH values experience a slight increase and stabilize at a pH of about 2.

The experiment has been repeated by changing the quantitative ratio between the solid sample (about 2,5g) and the distilled water (about 50ml). Whereas in the first experiment the pH decreased from the

leachates of the first leaching process, towards the leachates of the third leaching process, the present experiment showed an increasing of pH values in the same order. On the other hand, the shape of curves associated to the variation of pH in time is completely different from those of the first experiment, revealing a rather constant behavior of pH values. A tendency to a slight increasing of pH after 120 hours has been recorded.

Table 2 presents the variation of pH data in the first 24 hours after each leaching process. These values are almost analogous to those presented by Hammarstrom et al. (2005) for the eastern part of US, concerning the behavior of natural leachates in the same span of time.

Table 2 The variation of pH mean data in the first 24 hours after each leaching process

Sample	pH		
	1 st leaching	2 nd leaching	3 ^d leaching
220a	2.54	2.75	2.31
222	3.33	3.58	4.38
223	3.48	3.89	4.61
225	2.99	2.72	2.96
226	3.14	2.96	4.02

The Eh of leachates has been measured using the same MeterLab PHM 250 Ion Analyzer – Corning M555; Eh data range between 201 and 310mV. These values as well as the pH ranging between 2.2 and 3.5 show the presence of Fe^{2+} species in leachates (Pourbaix diagrams for iron solutions).

The experiments performed on secondary mineral formations from Balan mining perimeter lead to some preliminary conclusions, as follows:

The color of leachates resulted from the leaching of AMD natural products with distilled water is the result of the presence of some cations in solution of leachates, especially Fe^{3+} and Al^{3+} .

The artificial leachates have strong acid features (pH = 1.6-3.5), that match to those of natural leachates. These small pH data last for the first 24 hours after the leaching process, at least. After that period of time, Fe^{3+} species precipitate, allowing a slight pH increasing to about pH = 2, when it stabilize.

The grain size of the solid AMD products is in some sort responsible of the pH values; as expected, smallest grains undergo a much stronger dissolution than the largest ones,

aspect that explain the higher acidity of leachates emerged by the leaching of the smallest grains. The grain size of the solid AMD products plays a role in the acidity only in the case of the first leaching process.

During the leaching processes at lower quantitative ratios between the solid sample and the distilled water, the pH is relatively low and stable; the first leaching process generates the most acid leachates.

Eh-pH data show the presence of Fe^{2+} species in leachate solutions, while Fe^{3+} species precipitate as a solid brownish product.

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VARIATIONS OF METALS CONTENTS IN SOILS AND SEDIMENTS (MEKNES REGION, CENTRAL MOROCCO)

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1 Introduction

The present works focus about spatial distribution and temporal variations (between June 2001 and October 2003) of heavy metals in three different soils which each of them is irrigated by one of the three rivers (Boufekrane, Bou-Ishac or Ouislane) passing through the Meknes region.

2 Study area

The soil-collected samples came from agricultural areas. For spatial monitoring, the soil samples were collected from 3 locations; each of them is irrigated by one of the three rivers passing through the city of Meknes (Boufekrane, Bou-Ishac and Ouislane). For each locations, five samples were collected, one on each 20 cm deep; this gave a total of 15 samples.

The sediment samples were collected from the bottom of the three studied rivers. During the sampling, we avoided to collect the sediments located at the border of the rivers, so the sediments were collected in the medium of each river at the place where the water current was slow; a sample of 20 cm thickness was thus collected.

For temporal monitoring, soil and sediment samples were collected in June 2001 and October 2003. The Oued Boufekrane River takes its source about 30 km upstream, southern the city of Meknes (central Morocco) and joins the two other confluent (Bou-Ishac in the west and Ouislane in the east of the city of Meknes) about 20 km downstream. The water of these rivers, used in the irrigation of various cultures, is loaded by domestic and industrial wastewaters. These wastewaters are potentially harmful because of the rejections of the artisanal tanneries and potteries located inside the city of Meknes, and to industrial activities (paper-mill, chemical and food industries) located at the outlier periphery of the city of Meknes.

3 Soil samples

Fig.1 shows the enrichment factors of several elements (Al, Cr, Fe, Ni, Cu, Zn and Pb) measured in soil samples throughout the studied area. Al, Fe, Cr and Ni enrichment factor profiles of 2003 with respect to 2001 show similar features throughout the studied area with a high peak (523.16 % for Al, 315.58 % for Fe and 450.72 % for Ni) at site 7 located downstream of pottery industries.

In the same way, Cu and Zn enrichment factors profiles show identical features throughout the collected sites. In 2003, the contents of these two heavy metals have considerably increased with respect to 2001 in almost all the studied sites with high and significant peak at site 2 (181.25 % for Cu and 383.64 % for Zn) and at site 8 (80.23 % for Cu and 305.35 % for Zn). These two sites are located downstream the urban agglomerations.

The similar features for enrichment factors of Al, Cr, Fe and Ni in the first part and Cu and Zn in the second part are supported by the very significant correlations found between the elements of each group. These results suggest that Al, Cr, Fe and Ni in the first part and Cu and Zn in the second part have identical source in the collected sites.

Pb enrichment factor profile shows a distinct behaviour from the other metals. High Pb enrichment in 2003 with respect to 2001 (491.32 %) was recorded at site 5 located inside the city of Meknes.

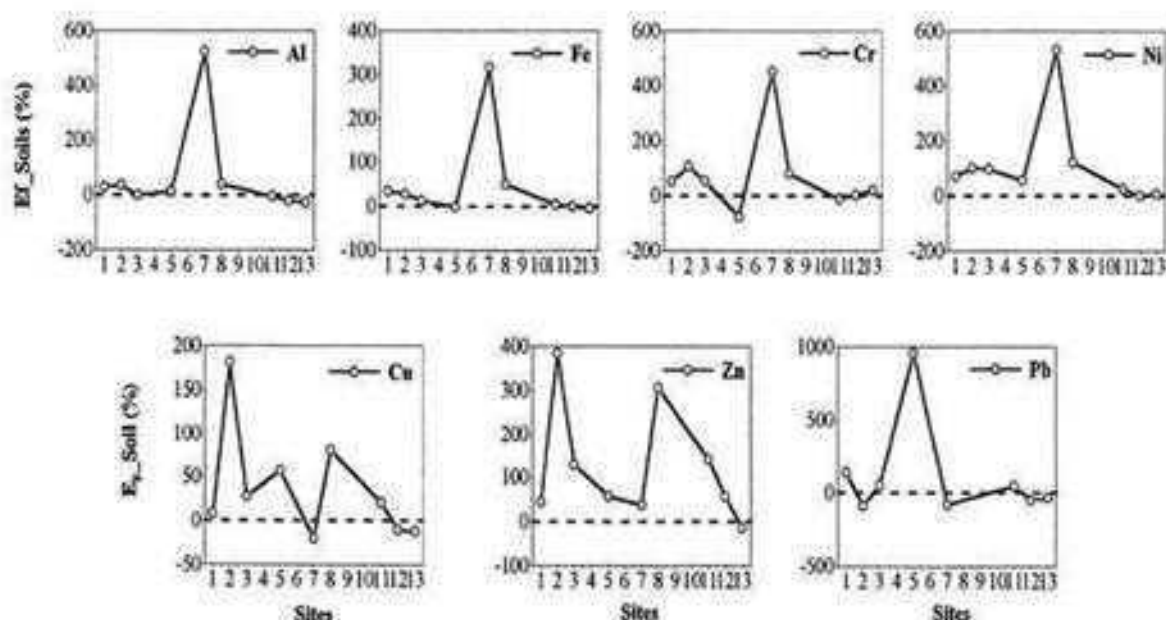


Fig.1. Metal enrichment in 2003 with respect to 2001 in soil samples of Meknes region.

4 Sediment samples

The enrichment factors of metal contents in sediment samples, in 2003 with respect to 2001, are shown in Fig.2.

The enrichment of Al, in 2003 with respect to 2001, has a factor of 63.37 % at site 3 located close to Ibn Rochd health centre, decreasing gradually to values close or under zero in the other sites with a marked enrichment (244.62 %) in the vicinity of pottery activities (site 6). The E_F^s of Fe and Cr show a low enrichment for almost all the sites except for an enrichment of 116.08 % for Cr at site 3 and of 172.56 % for Fe at site 6 located in the vicinity of pottery activities. Ni presents E_F values close to 80 % at sites 3, 5 and 8 (79.63, 76.74 and 89.29 % respectively) located downstream the urban agglomerations for sites 3 and 8, and inside the city of Meknes for site 5. Furthermore, site 6 indicates an increase of 135.56 % in the E_F of Ni. Pb and Zn show a significant enrichment at site 3 (358.99 % for Zn and 426.56 % for Pb) and site 8 (223.84 % for Zn and 231.38 % for Pb). Zn also presents E_F values of 100 % at site 5 and 197.40 % at site 7 located downstream the pottery activities. The E_F calculated for Cu indicates an irregular behaviour throughout the region with enrichment in almost all sites; the E_F values of 77.78, 46.88 and 65 % are respectively recorded at sites 6, 12 and 13 with a marked enrichment at site 3 (105.15 %) and site 8 (119.46 %).

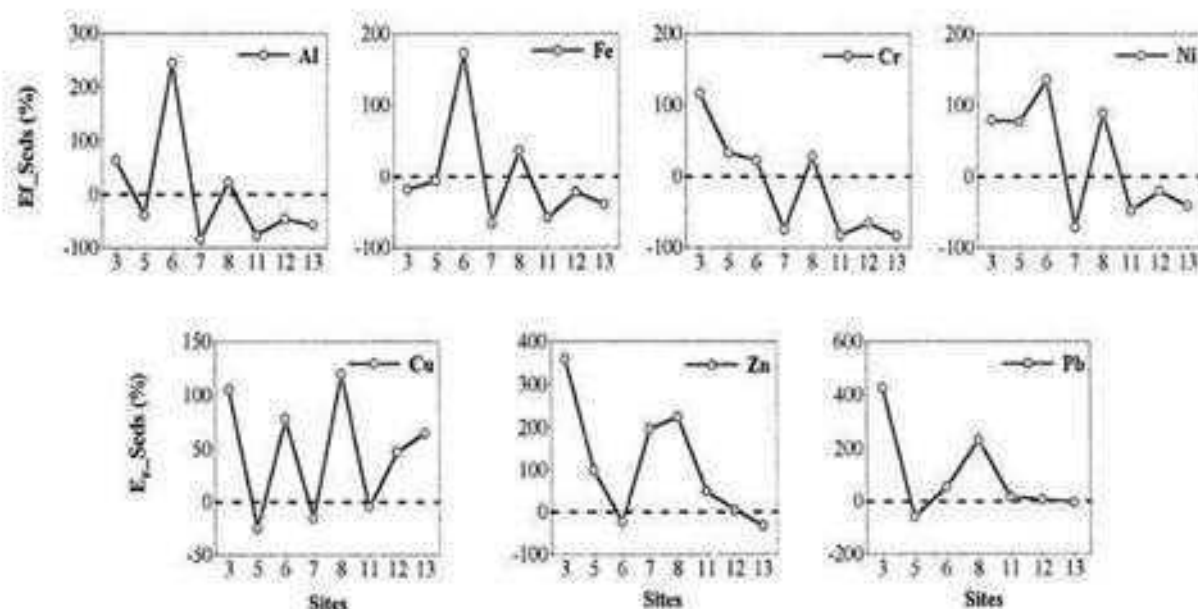


Fig.2. Metal enrichment factors in 2003 with respect to 2001 in sediment samples of Meknes region.

An increase in the metal contents of Al, Cr, Fe, Ni, Cu, Zn and Pb is observed in 2003 with respect to 2001. This increase is more significant and marked at some sites than the other mainly at sites 3, 6, and 8. The magnitude of enrichment of the studied metals is different. The difference in the magnitude of enrichment may be caused by several reasons such as the differences in the magnitude of input for each metal from the Meknes region, and/or differences in the removal rate of each metal, and/or differences in sampling season (June for 2001 and October for 2003) (Villaescusa-Celaya et al., 2000; Morel et al., 1975).

5 Conclusion

The spatial study of Al, Cr, Fe, Ni, Cu, Zn and Pb contents in Boufekrane, Bou-Ishac and Ouislane soils shows a homogeneous depth concentration distribution for almost all metals except for Cr and Pb in Bou-Ishac soils. The highest Cr and Pb concentrations recorded in the superficial layer of Bou-Ishac soils indicate a contribution of anthropogenic source.

The metal contents from 2001 to 2003 have increased in soil and sediment samples throughout the studied area. This enrichment is more significant in sediment than in soil samples and it is more marked in some sites than the other. The enriched sites have the features to be close to urban agglomerations or industrial activities especially pottery activities.

Acknowledgments

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SPATIAL VARIATIONS OF METALS CONTENTS IN SOILS AND ROAD TRAFFIC IMPACT (MEKNES REGION, CENTRAL MOROCCO)

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1. Introduction

The aims of the present works are:

- to evaluate the spatial distribution of seven metals (Al, Cr, Fe, Ni, Cu, Zn and Pb) in three different soils which each of them is irrigated by one of the three rivers (Boufekrane, Bou-Ishac or Ouislane) passing through the Meknes region;
- to determine the spread of road traffic impact on Pb concentrations in soils located at the vicinity of a main highway.

2 Study area

The soil-collected samples are coming from agricultural areas. For the sample location and area presentation, see Tahri et al. (this volume, previous paper).

3 Analysis of metals

After collection, soil and sediment samples were dried at 60 °C during 24 hours and ground in a grinding device. Then 2.5 g of crushed samples was calcinated at 960 °C during 2 hours. After cooling, the samples were weighted again and the losses on ignition (LOI) were determined. The major element contents, for soil and sediment samples were determined by WD-XRF spectrometry using a SRS 3400 spectrometer. The metal concentrations were determined using the Wavelength Dispersive X-Ray Energy (WD-XRF) for major elements and Inductively Coupled Plasma Emission Spectroscopy (ICP-AES) for trace elements. These analyses were carried out at "Ecole des Mines de Saint-Etienne" in France. Previously, the soil and sediment samples were digested with a classical triacid (HCl, HNO₃, HF) decomposition procedure.

4 Spatial variations of metal contents in soil samples

In Boufekrane soils, the coefficient of variation CV values of Al, Cr, Fe, Ni, Cu, Zn and Pb range between 1.47 and 42.12 % indicating a relative homogeneous distribution of

these depth metal concentration profiles. In Bou-Ishac soils, the CV values are low for Al, Fe, Cu and Ni (between 13.81 and 33.75 %) indicating a relative homogeneous distribution of these depth metal concentration profiles; and high for Zn (52.93 %), Cr (69.34 %) and Pb (101.63 %) attributed to the high concentrations measured at the superficial layer (252 $\mu\text{g/g}$ for Zn, 276 $\mu\text{g/g}$ for Cr and 71.1 $\mu\text{g/g}$ for Pb). The correlations could indicate that the Zn, Cr and Pb have the same origin in the studied area. In the Ouislane soils, the CV values of Al, Cr, Fe, Ni, Cu, Zn and Pb ranging between 4.30 and 45.83 % indicate a homogeneous distribution of these depth element concentration profiles.

These conclusions are supported by the profiles displayed by the plots of concentration, for each element, against depth. For all the studied elements, the profile distributions show a low variation throughout the depth, except for Cr, Zn and Pb in Bou-Ishac soils (Fig.1) which indicate a high concentration in the superficial layer with respect to the deep layers. These high superficial concentrations indicate the contribution of anthropogenic sources.

The comparison of the metal contents between Boufekrane, Bou-Ishac and Ouislane soils indicates that the highest concentrations, for almost all metals, are recorded in Ouislane soils. As it is indicated by the homogeneous depth concentration profiles (Fig.1), these highest concentrations, compared to Boufekrane and Bou-Ishac soils, could be due to natural geology of this site.

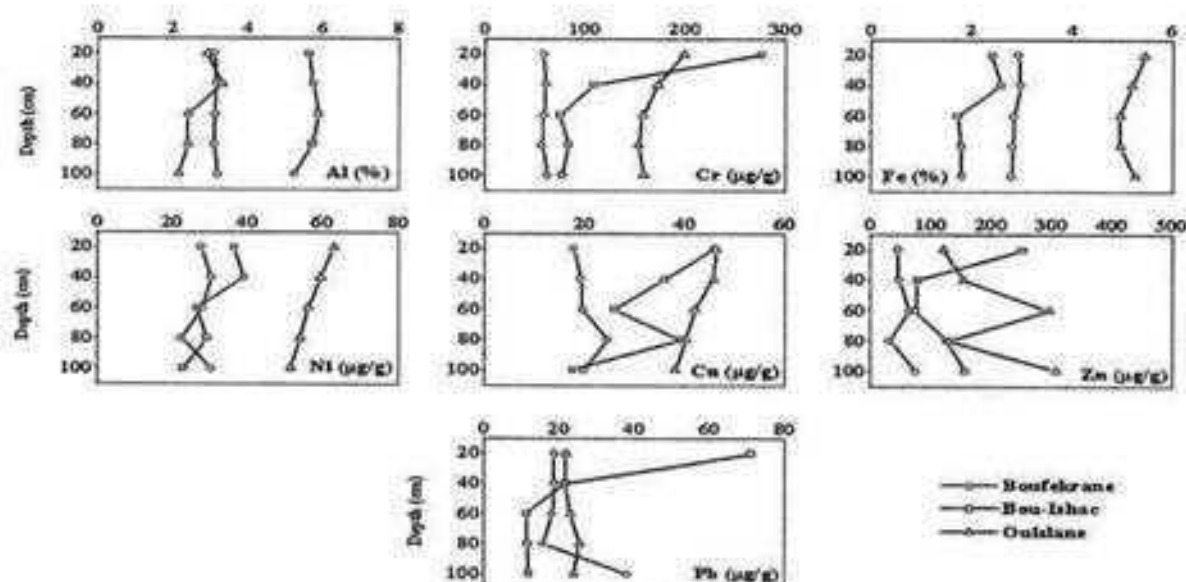


Fig.1. Depth concentration profiles of Al, Cr, Fe, Ni, Cu, Zn and Pb in Boufekrane, Bou-Ishac and Ouislane soil samples.

5 Variations of Pb concentrations with distance from main highway

The impact of road traffic on Pb concentrations was confirmed and established by many studies (e.g.: Xiangdong et al., 2000). We try to evaluate the spread of this impact on soil samples located in the vicinity of a main highway. To accomplish this goal, a set of soil samples was collected at different distances from a main highway. The obtained measures are illustrated in Fig.2; the point noted as 0 corresponds to a main highway. The Pb concentrations show strong dependence on the distance from the main highway. Figure 2a shows that after 200 m, the Pb concentrations decrease significantly (from 444 mg/g in the vicinity of the main highway to 19 μ g/g at 200 m) and become stable: further on the impact of road traffic on Pb concentrations becomes not significant or non-existent.

A second sampling was made on another main highway, but this time for the first 100 m from the main highway, we have tried to take a soil sample at each 50 m. As it is showed in Fig.2b, the Pb concentrations decrease by half after 50 m from the main highway (244 μ g/g at point 0 and 129 μ g/g at 50 m), by about the fourth after 100 m (52.6 μ g/g) and become stable after 200 m. The impact of the road traffic on Pb concentrations in soils depends strongly on the distance from the main highway. This impact is more significant in soils located in the vicinity of the main highway.

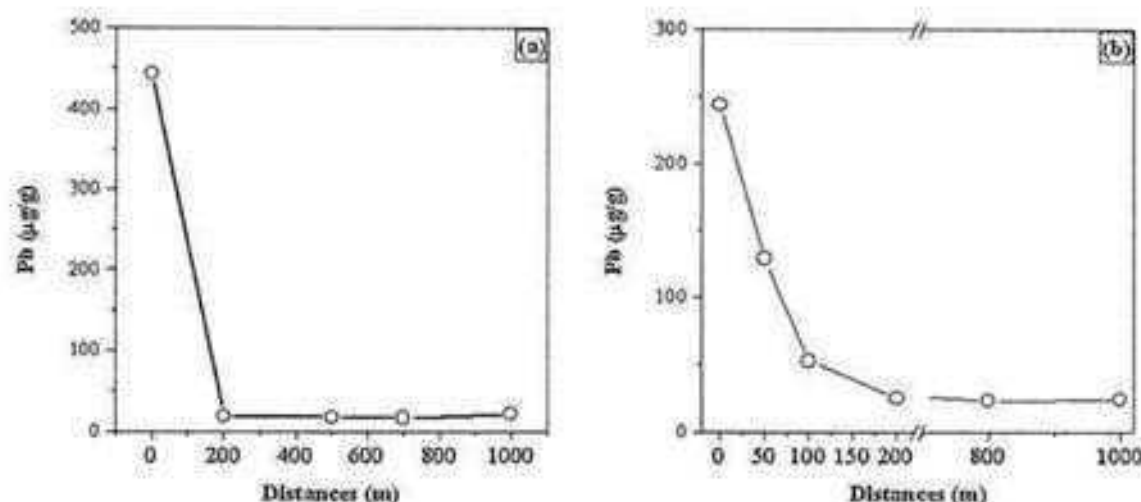


Fig.2. Pb concentrations at different distances from two different main highways.

6 Conclusion

The spatial study of Al, Cr, Fe, Ni, Cu, Zn and Pb contents in Boufekrane, Bou-Ishac and Ouislane soils shows a homogeneous depth concentration distribution for almost all metals except for Cr and Pb in Bou-Ishac soils. The highest Cr and Pb concentrations recorded in the superficial layer of Bou-Ishac soils indicate a contribution of anthropogenic source.

The impact of road traffic on Pb concentrations in soil samples showed strong dependence on distance from a main highway. In this study, we have found that this impact decreases after 50 m and becomes insignificant or non-existent after 200 m from the main highway. This observation can be affirmed by collecting soil sample at each 10 or 5 m to evaluate the spread interval of the road traffic impact.

Acknowledgments

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REVIEW OF MAGNESITE DEPOSITS IN IRAN

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Abstract: The magnesite deposits are grouped in two main areas in Iran: South Khorasan, Sistan and Baluchestan provinces. This paper characterizes individual deposits from the viewpoint of their resources, geological setting, genesis, mineralogy and processing. The main problem for producers of magnesite in Iran is connected with beneficiation of magnesite ore to increase MgO content up to 90-92 % and exploration blind of magnesite deposits. The magnesite deposit Houz-Sefid and Torshak are treated in more details.

Key words: Technological mapping, cryptocrystalline magnesite, Houz-Sefid deposit

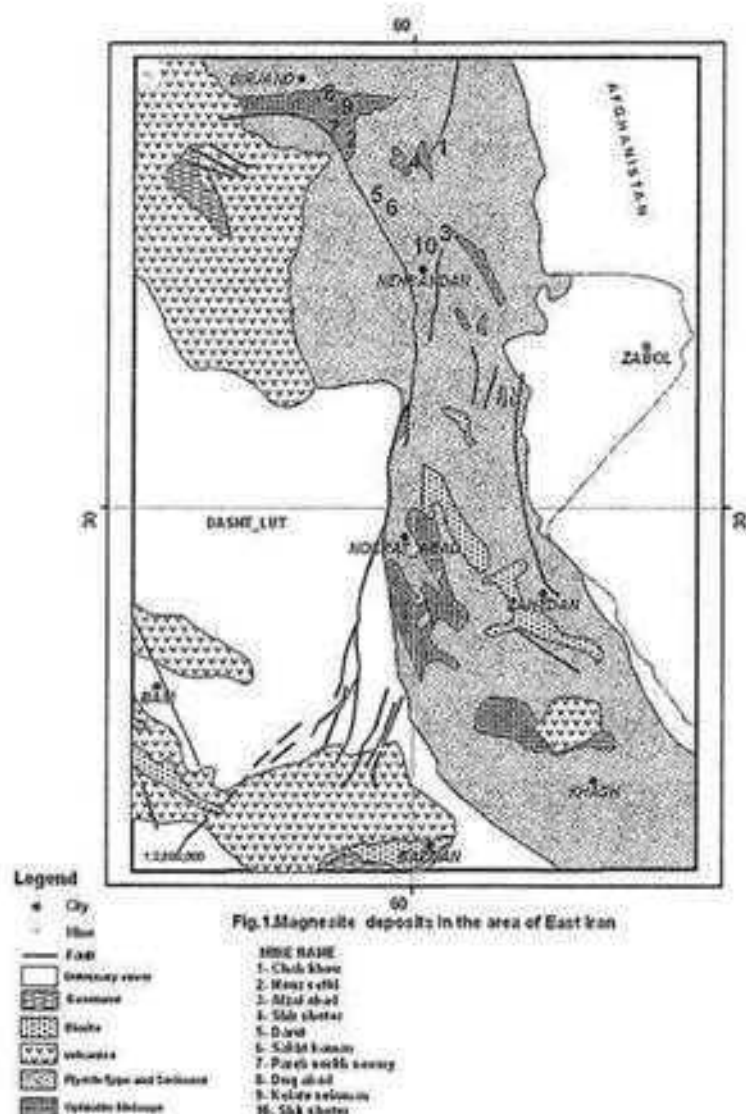
1- Introduction

The magnesite deposits in Iran are grouped in the areas of Khorasan, Sistan and Baluchestan. There are about 20 explored deposits with proven resources, nearly 80% of the deposits are located in Khorasan, and 20% are in Sistan and Baluchestan. The estimated total resources of 3.5 million t are an approximation based largely on geology evidence. About 2.5 million t of this amount is related to low grade magnesite (16 deposits of 20). At present time, only two deposits in East Iran are being mined. They are mined by open pit methods and the possibility of underground mining is considered for Houz-Sefid deposit (Fig.1).

Sinter magnesia plant is located south of Birjand with a production capacity of 30,000 tpa. dead-Burned magnesia is produced in various grade from 88%-96% MgO and grain size from 0-25 mm according to application. Magnesites were sampled at the Houz-Sefid, Torshab deposits and the factory dumps.

2-Geology setting:

Magnesite deposits occur in serpentine and other ultrabasic rocks which belong to ophiolitic belts of eastern Iran. Here magnesite occurs as veins and lenses. The veins cross each other forming stockwork. An amorphous magnesite is associated with karnalite, nontronite, opal, and hydrous ferric oxides. It seems that the volcanism in eastern Iran is most important factor to provide energy for mineralization (Abedi, 1999).



3-Genesis:

The study of magnesite deposits genesis in eastern part of Iran, spatially connected with ultrabasites, gives an additional material to understand the behavior of Mg under different physico-chemical conditions during decomposition of magnesian rocks and subsequent removing and sedimentation. The magnesite can occur not only in parent ultrabasites, but also in the surrounding rocks near ultrabasic massive. The surrounding rocks can be considered as flysch and volcanic-sedimentary terrains. Magnesites of this type have cryptocrystalline structure: magnesite crystals of tiny size are seen only by using electron microscope. There are also magnesites related to late formation of listvenites. The younger magnesites are more pure than the older ones (Abedi, 1999; Nasedkin, 2003).

4-Mineralogy:

All inspected deposits are characterized by different composition and structural features of magnesite ores. Consequently, individual approach is necessary for each deposit. The MgO content is relatively constant in one sample. The MgO contents can vary from 60 to 96 %

(average, 75-78 %). The size of local areas is 0.05-0.1 mm. The admixtures in magnesite ore can be divided into 2 types: macro-and micro-admixtures. Macro-admixtures size is of 10-30 mm. The micro-admixtures consist of amorphous silica, quartz, talc, muscovite and dolomite. The grain size is 10-30 mm. SiO_2 and CaO present the main destructive micro-admixtures. Silica is included in the following minerals: amorphous SiO_2 (50-60 mm), quartz (10-20mm), talc (20-30 mm), serpentine, and muscovite. CaO is a part of dolomite and rarely of calcite.

4-1) Magnesite from Torshak deposit is characterized by different admixtures. Magnesite ore of central part has some high MgO content up to 77-92%. Magnesite ore from central and marginal parts of deposit was collected for investigation. One probe was collected on the southern flank of deposit after primary crushing. The total weight of the probe is about 10 kg. The probe was divided by hand and separated into 6 varieties: a, b, c, d, e, f (Table2).

Table 2. Petrographical composition of one probe (Torshak deposit)

	Rock	% MgO	% SiO_2	% CaO	variety	weight	
						Kg	%
1	Massive magnesite (white)	90-91	2.8-3.2	2.2-2.5	a.	4.6	45.1
2	Brecciated magnesite (white)	68-70	10-15	7-10	b.	4.7	46.1
3	Mylonite with chlorite-dolomite cement	40	25	15	c.	0.2	2.0
4	Ultrabasic breccia with secondary magnesite and dolomite	55-65	20-22	12-18	d.	0.1	1.0
5	Mylonite with magnesite-dolomite cement	58-60	18-20	15-20	e.	0.1	1.0
6	Mylonite oriented structure with chlorite- serpentine cement	25-30	40-50	15-20	f.	0.5	4.9
7	Total				a-f	10.2	100.

4-2) Magnesite crystals have rounded apexes. The size of crystals is of 5-10 micrometers. Average content of admixture mineral reaches 10-15 %, contains inclusions of talc, dolomite, quartz, amorphous SiO_2 .

4-3) Characteristics of the dump in the Sinter magnesia plant; the sample was collected directly in plant from crushed product prepared for burning. The fraction 10-20 mm in size was separated. The main part of the sample is presented by plate-like rectangular crystals of magnesite, often with minor admixture of CaO and SiO_2 . The size of crystals is 1-5 mm and less. Segregations of ultra-fine particles of amorphous SiO_2 , dolomite crystals and flakes of muscovite are also presented. The silica content can reach 6-12%. The dolomite content is not constant. It varies from 2 to 5 %.

6-Recommendation and Conclusion:

The experience of cryptocrystalline magnesite in Halilov (Ural), for economic processing of these deposits the application of these stages is recommended. However the processing branch in that area can only process the magnesite with grade of up to 90 %, the two main following recommendations may be essential. All inspected deposits are characterized by different composition and structural features of magnesite ores. Consequently, individual approach is necessary for each deposit. The MgO content is not relatively constant in one sample. The MgO content can vary from 60 to 96% (average, 75-88%). The size of local areas is 0.05-0.1 mm. The admixtures in magnesite ore can be divided into 2 types: macro- and micro-admixtures. Macro-admixtures (5-30 mm) are represented by aggregates of several minerals: serpentine, chlorite, dolomite, magnesite, quartz. Micro-admixtures (10-300 mm) consist of amorphous silica, quartz, talc, muscovite, and dolomite. Magnesite ores with different MgO and admixture content can be outlined in blocks. The size of blocks can reach 20-100m and more in length. Such blocks can be separately mined. The technological mapping is necessary to isolate the blocks with high content of MgO, up to 90-92%. The technological mapping includes detailed sampling with geochemical exploration methods in GIS environment.

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MINERAL POTENTIAL MAPPING OF HIDDEN MAGNESITE BASED ON LITHOGEOCHEMICAL EXPLORATION AND GIS ANALYSIS IN EAST OF IRAN

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Abstract

In this paper a model for hidden anomaly recognition in a regional geochemical exploration was investigated by using synthesis of geological, geochemical and ETM⁺ data, based on GIS technology. Geochemical modeling built up according to the results of study of chemical elements distribution pattern in ores and primary halos from Hoze-sefid deposits. Lithogeochemical methods were used here beside GIS to find variables that can be used as geochemical indicators of regions with prediction of magnesite hidden ore bodies.

Key-Words: - Cryptocrystalline magnesite, GIS, Multiplicative zonality coefficient

1-Introduction

We can find magnesite as crystalline and cryptocrystalline forms but the majority of known deposits in Iran are represented with cryptocrystalline (amorphous) type. The crystalline type is too limited and occurs in vein form. The main occurrence of magnesite deposit is in the ultramafic rocks. The deposits of cryptocrystalline magnesite are known in many countries of the world such as Greece, Russia (Urals) and Iran. The output of cryptocrystalline magnesite have reached about 20% from total volume of production of magnesite raw material in the world (Tatarinov, 1969; Nasedkin, 2003). They are two different opinions on the origin of amorphous magnesite. Russian geologists traditionally consider amorphous magnesites as the products of ultrabasic rocks weathering (Tatarinov, 1969). However, another large group of investigators considers amorphous magnesites to be typical for hydrothermal formation (Maksimovic and Dangic, 1974). 170 occurrences have been listed for in Khorasan, some of them exploited and others not. In Iran, there are about 20 explored deposits with proven resources, nearly 80% of the deposits are located in Khorasan, and 20% are in Sistan and Bluchestan. The estimated total resources of 3.5 million t are an approximation based largely on geology evidence. About 2.5 M t of this amount is related to low grade magnesite (16 deposits of 20). At present time, only two deposits in East of Iran are being mined. They are mined by open pit methods and the possibility of underground mining is considered for Houz-Sefid deposit (BRGM report, 1978).

2-Geological setting:

The tectonic feature of eastern parts of Iran is very complicated. Magnesite deposits occur in serpentinites and other ultrabasic rocks which belong to ophiolitic belts of eastern Iran. Here magnesite occurs as veins and lenses. The veins cross each other forming stockwork. An amorphous magnesite is associated with karnalite, nontronite, opal, and hydrous ferric oxides (Abedi, 1999). The characteristics of magnesites of eastern part of Iran are as follows:

1) Quality (degree of purity and chemical composition) of magnesites is varying in length and depth. 2) On the bases of core drilling and analyses of different types of sample clearly it can be seen that silica percentage is decreasing from surface to depth. 3) Continuous tectonic activity and hydrothermal cycle are seen in all magnesite regions since long time before (which they are evidences of older listvenite than magnesites) and also at the present time the same phenomena are going on in lesser amount. 4) Along with main fault of area that they have acted as a transform zone, Neogene magmatism with calc-alkaline composition is evidence of active plate margin that it can be one of the active agent of ground water and activation of hydrothermal energy that it has been source of CO₂, that it is essential part for formation of magnesites. Mainly the magnesite anomalies of eastern parts of Iran are small and their deposits are varying between hundred to few hundred thousand tons. 5) The minus 150 μ m (-100 mesh) fraction of stream sediments was shown to be the optimum grain size fraction in the mountainous area.

2. Methodology

In this section we first explain the geochemical exploration models used to recognize blind anomalies in regional exploration (Grigorian, 1992). Then lithogeochemical method and remote sensing of techniques were used for prospectivity modeling in GIS environment.

2.1 Geochemical exploration models

The study of concentration characteristics of some trace elements, such as Zn, B, Mo, Cu, Fe, Co, Mn, Ba, Fe, as well as lithogeochemical surveys of different typical magnesite deposits, provide a basis for determining the geochemical background values and thresholds of anomaly, as well as the knowledge of association of characteristic element in different geological bodies and offer the basis for evaluation of anomaly and along with the fundamental information for determining the source bed of ore deposit. Moreover, the follow-up check moderately intensive Zn, B, Mo, Cu, (sub-ore) and Co, Mn, Ba, Fe (supra-ore) multiplicative halos in lithogeochemical survey often leads to the discovery of some magnesite mineralized bodies. For example, Houz-Sefid deposit has also been shown on the surface over a large blind magnesite deposit in eastern Iran. Therefore, Zn.B.Cu.Mo blind anomaly can usually be found in spite of the type of magnesite deposit when coefficient of

contrast $K = (Zn.B.Cu.Mo / Co.Mn.Ba.Fe)$ in lithogeochemical survey is applied for reconnaissance. With regard to hydrothermal deposit, vertical zoning of element concentration and association often happen simultaneously when the ore-bearing fluid intrudes into fractures and forms ore deposit, which makes it possible for itself to be applied in prospecting of blind ore bodies and evaluation of its degree of denudation. Through probability statistics on axial zoning sequence for primary halo indicator elements from typical hidden magnesite deposits (Hoz-Sefid), we have the comprehensive zoning sequence from upper to lower as: Zn-B-Mo-Cu-Fe-Co-Mn - Ba. Statistical result shows that each deposit has specific parameters of element or multiplicative ratios. A comparison between values of multiplicative zonality coefficient, for example $K_1 = (Zn.B.Cu.Mo/Co.Mn.Ba.Fe)$ and $K_2 = (Zn.B/Mn.Ba)$ reflect the vertical geochemical zonality in the structure of primary geochemical anomalies. Index K_1 is showing the best detection in geochemical halo.

Table1. Multiplicative coefficient of zonality values in Houz-Sefid ore deposit

Level(m)	Zn	B	Co	Mo	Cu	Fe	Mn	Ba	K_1	K_2
0	160	45	50	0.5	17	46000	460	110	5.10^{-7}	0.14
40	37	9	53	0.3	20	54000	600	153	7.10^{-9}	4.10^{-3}
100	35	15	100	0.6	30	90000	1500	700	1.10^{-9}	5.10^{-7}
ratio	4.57	3	0.5	0.8	0.57	0.51	0.31	0.16	<u>500</u>	280

2.2 Application of GIS and remote sensing

In applying GIS to the mapping of mineral potential, deposit models play a role both in the selection and derivation of maps that are likely to be good predictors of the deposit-type under consideration, and for the assignment of weights to the various predictor maps (Ziaii & Abedi, 2004). In order to assess the mineral potential mapping of blind magnesite based on lithogeochemical exploration and GIS analysis in East Iran, aerial stream-sediment and ETM+ data are used. Ratio image of bands 5/7, 3/1, 4/3 were chosen and transferred into ArcGis-9. Barren zone were calculated by using ArcGIS function (Fig. 1).

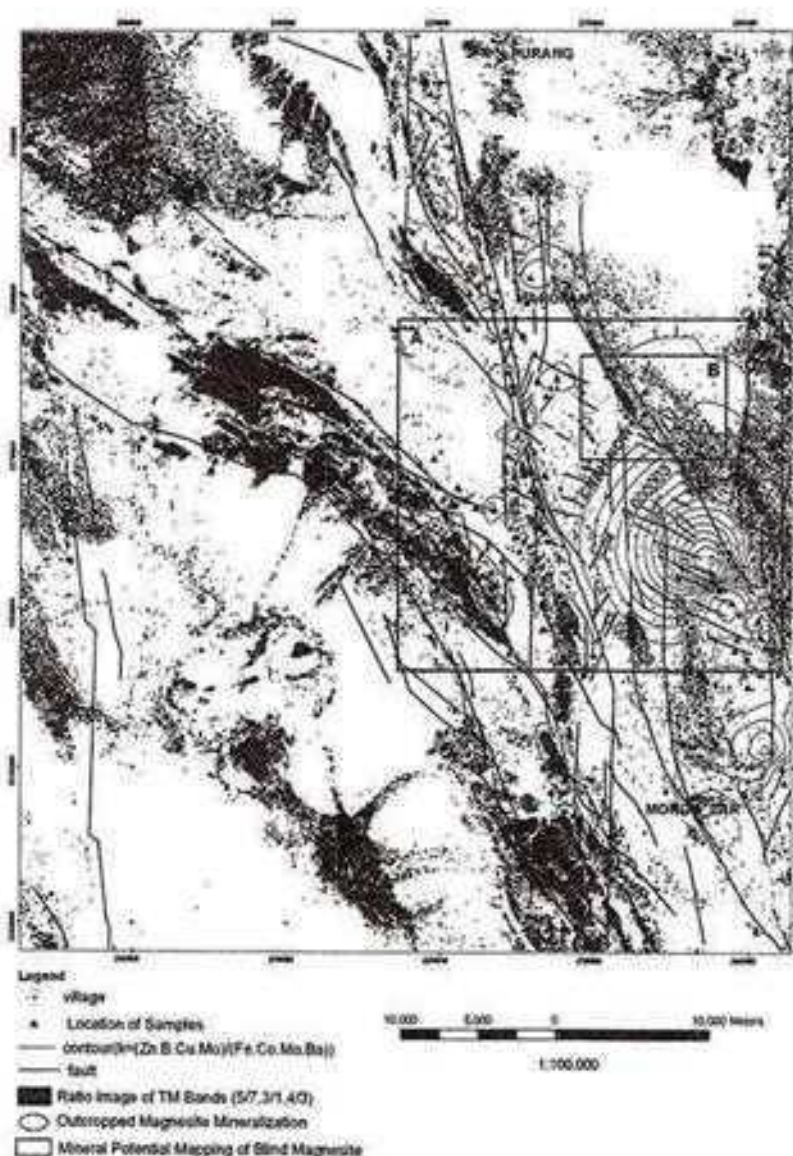
3- Conclusion

The use of lithogeochemical method such as the vertical geochemical zonality (K_1 and K_2) provides numerical and graphical means through which the relationship of the indicator-elements and samples can be studied (Table 1, Fig.1). These methods were used here beside GIS to find variables that can be used as geochemical indicators of regions with magnesite deposits. In conclusion zone A and B (Fig.1) are suggesting for mineral potential mapping of blind magnesite based on lithogeochemical exploration on the scale of 1:20000.

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Fig. 1. Mineral potential mapping of blind magnesite deposits in East Iran



MINERALOGY AND PETROGRAPHY

**PRELIMINARY DATA ON SOME PHOSPHATES FROM
CONȚU-NEGOVANU PEGMATITES (LOTRU-CIBIN MTS.)**

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Keywords: *apatite, triphylite-lithiophilite, albite-spodumene pegmatites, feldspar-mica pegmatites, Sebeș-Lotru Group, XRF, EMPA, ICP-MS.*

Previous research carried out on the specific minerals belonging to the Conțu-Negovanu pegmatites (Săbău *et al.*, 1987) emphasised the presence of phosphates such as apatite, triphylite-lithiophilite, heterosite-purpurite, amblygonite-montebrazite, hureaulite, tavorite. Phosphates are usually present in both pegmatite types occurring in this area and display a great compositional complexity, typical for the granitic pegmatite phosphates and especially for the rare element pegmatite phosphates.

The Conțu-Negovanu pegmatite field is located within the central-western part of the Southern Carpathians, on the slopes of Conțu river, a tributary to Sadu river. The pegmatites are hosted by mesometamorphic rocks belonging to the Sebeș-Lotru Group, which is the most extended lithostratigraphic entity of the Getic Crystalline Realm. The Sebeș-Lotru sequence represents a crustal fragment of Cadomian-Caledonian age, part of an active continental margin or an island arc near a continent. Possibly, around 430 M.a., this terrain collided with an ahead block, being consequently involved in a subduction process (Balintoni *et al.*, 2004). The genesis of the Conțu-Negovanu pegmatites is considered to be metamorphic, as they seem to have originated mainly, if not entirely, as a result of segregation within a fluid under preanatectic conditions (Săbău *et al.*, 1987). Beside the albite-spodumene pegmatites (or lithian pegmatites – LPs), in the Conțu-Negovanu field are also present common feldspar-mica pegmatites (FPs). The mineralogical composition, as well as the bulk chemistry features and geochemical signatures suggest their affiliation to two distinct pegmatite classes, according to Černý's (1992) systematic classification of pegmatites: (a) rare-element class and (b) muscovite class, respectively (Murariu, 2001). FPs are of *ceramic and mica-bearing type*,

being barren or poorly mineralised (Li, Be, Ti, Nb, Ta, U, Th, Y, REE); the LPs are assigned to one of the five subdivision types of the rare-element class: the *albite-spodumene type*, characterised by minor to extensive mineralisation (Li, Rb, Cs, Be, Ga, Y, REE, Sn, Ti, U, Th, Hf, Nb, Ta), with typical substantial Li and variable rare-alkali fractionation (Černý, 1992). The former consist of quartz + K-feldspar, plagioclase + muscovite $\pm$ biotite $\pm$ tourmaline $\pm$ garnet and also small amounts of staurolite, apatite, ilmenite, rutile *etc.*, whereas the latter present the typical mineral assemblage: albite (cleavelandite) + spodumene + quartz + muscovite and contain also subordinate amounts of microcline, biotite, garnet, apatite, kyanite, triphylite-lithiophilite, heterosite-purpurite, amblygonite-montebrazite, uraniferous magnocolumbite, hureaulite, tavorite *etc.* (Hann, 1987; Săbău *et al.*, 1987; Murariu, 2001).

Generally, our research (Androne, 2005), and this paper as well have been focused on apatite and the minerals belonging to the triphylite-lithiophilite series. All the quantitative investigations were performed in the laboratories of the Geological Institute of the „Albertus Magnus” University of Köln, Germany.

In X-ray fluorescence technique, bulk analyses were performed with a Philips PW 2400 X-ray spectrometer, using the analytical procedure called „oxiquant”. Seventy-two natural rocks and clays were used to determine the calibration curves of the pertinent elements.

EMPA were carried out with a JEOL JXA-8900 instrument, using an operating current of 20 nA and accelerating voltage of 20 kV. X-ray intensities of the alkalis, the minor (Ti and Mn) and the major elements were counted for 5s, 40s and 60s, respectively. In order to minimize losses of Na and K, the beam diameter was expanded to 10 mm. Components were standardised using natural minerals, glasses of natural rocks and synthetic oxide compounds. The results were corrected using the ZAF procedure (Reed, 1996).

The ICP-MS investigations were performed with a Perkin Elmer/Sciex ELAN 6000 ICP-MS (quadrupole mass spectrometer). Measurements of element concentrations were performed using as internal standards Ru-Re (10 ng/ml) to minimize drift effects and two calibration solutions (high purity chemical reagents). A batch of 5-7 samples was bracketed by two calibrations procedures. Accuracy and precision of determinations were checked with certified reference materials (CRM) (Dulski, 2000).

Apatite is present in the LPs as very small greenish crystals 0.02-2 mm in size, occasionally reaching 5-10 mm. It is usually developed in the albite-spodumene mass and may be directly associated with other phosphates. In the FPs, apatite was found only as

submicroscopic grains, generally detectible by EMPA (photo 1.). In this case, it is associated with quartz, feldspars and tourmaline, in the marginal zones of these pegmatites. The bulk chemical data of the apatite (table 1.) show normal values for P and Ca: the former ranges between 40.3-43.6 % P_2O_5 , being close to the values found by Smaranda Rădășanu (2000) in the apatite from the Preluca pegmatites (41.22-41.93 % P_2O_5), whereas the latter may present some lower values (48.26 % CaO, in sample Ap-881, asociated with higher Fe and Mn probably due to the triphylite-lithiophilite inclusions in this sample). From a structural perspective, apatite is characterized by the *A* sites, presenting both VII-fold and IX-fold coordination (Hughes and Rakovan, 2002) and being occupied by large ionic radius cations (Ca, Sr, Na, Mn, Fe^{2+} , Mg, REE, Pb) and the tetrahedral *X* sites, occupied especially by P, which may be substituted for by small ionic radius cations such as Si, S, As, V. The unit formulae indicate a deficit in the *A* site occupation, generally due to the minor element contents (on which we do not have analytical data yet) usually represented by REE and Y substituting for Ca in important amounts. The penetration of Mn, Fe^{2+} or Mg in the Ca sites is realised following simple substitution mechanisms, whereas the Na accomodation supposes the presence of other elements needed for the maintenance of the electrostatic balance. An exemple is the Al penetration in the apatite following the mechanism: $NaAlCa_2$ (Sha and Chappell, 1999).

Members of the **triphylite-lithiophilite** series occur only in the LPs, as gray-greenish irregular fine grained masses usually rimmed by brown or dark purple to black secondary phosphates which may belong to the heterosite-purpurite series (photo 2.). The chemical data (table 2.) generally show a large variation range of Fe and Mn. In the samples Ph-963 and Ph-964 these values are much higher, being also correlated with lower Li contents, a fact which suggests the formation of secondary heterosite-purpurite. The unit formulae usually show a slight deficite in the *X* site occupation, probably due to the presence of some minor elements (on which there are not available analytical data yet) substituting for P in these structural sites.

Table 1. Apatite chemical composition (wt. %) and unit formulae (a.p.f.u.)

oxides wt. (%)	Sample							
	Ap-141	Ap-142	Ap-143	Ap-881	Ap-961	Ap-962	Ap 5	Ap 9
SiO ₂	0,056	0,00	0,00	1,771	0,016	0,00	-	0,022
Al ₂ O ₃	0,041	0,00	0,012	0,014	0,00	0,00	0,002	-
TiO ₂	0,00	0,00	0,00	0,023	0,025	0,00	0,012	-
FeO	0,062*	0,06*	0,014*	4,00*	0,749*	0,16*	0,175	0,151
MgO	0,010	0,017	0,00	0,00	0,00	0,00	0,013	-
MnO	0,073	0,141	0,093	3,233	2,395	2,016	1,171	1,085
CaO	57,96	57,88	58,13	48,264	52,56	55,285	55,605	55,69
Na ₂ O	0,031	0,021	0,007	0,005	0,329	0,00	0,128	0,106
K ₂ O	0,00	0,00	0,00	0,00	0,00	0,002	0,005	0,032
P ₂ O ₅	42,40	43,43	43,60	40,374	40,305	42,748	41,22	41,93
Number of ions on the basis of 12 (O,OH) (a.p.f.u.)								
P	2,830	2,862	2,864	2,794	2,866	2,831	2,827	2,846
Si	0,004	0,00	0,00	0,145	0,00	0,001	0,00	0,002
X	2,834	2,862	2,864	2,939	2,866	2,832	2,827	2,847
Fe	0,004	0,004	0,008	0,273	0,011	0,052	0,012	0,010
Mg	0,001	0,002	0,00	0,00	0,00	0,00	0,002	0,00
Mn	0,005	0,009	0,006	0,224	0,135	0,168	0,080	0,074
Ca	4,897	4,828	4,832	4,227	4,690	4,672	4,826	4,784
Na	0,005	0,003	0,001	0,00	0,00	0,053	0,020	0,016
A	4,912	4,846	4,847	4,724	4,836	4,945	4,940	4,887

- undetermined; * - FeO as total iron; (Ap-141) - (Ap-143) - apatite associated with tourmaline, albite, microcline and quartz, in FPs; (Ap-881) - apatite associated with muscovite, albite and Li, Fe, Mn phosphates (lithiophilite - triphylite), in LPs; (Ap-961) - (Ap-962) - apatite associated with spodumene, quartz and Li, Fe, Mn phosphates (lithiophilite - triphylite), in LPs; (Ap 5) - (Ap-9) - apatite from Preluca pegmatitic subprovince (Smaranda Rădăşanu, 2000).

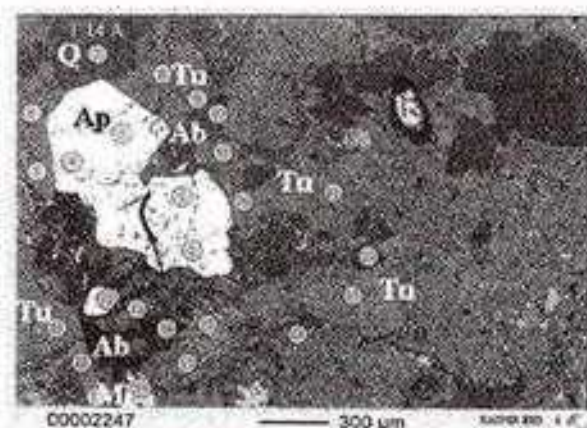


Photo 1. EMPA image (Ap – apatite; Q – quartz; with Tu – tourmaline; Ab – albite ; Mi – microcline).

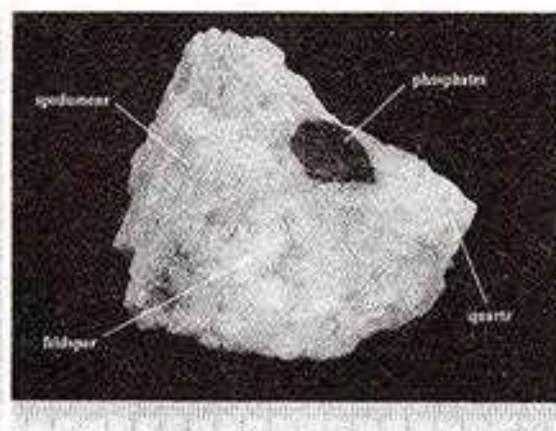


Photo 2. Li, Mn phosphates associated with spodumene, feldspar and quartz.

Table 2. Lithiophilite – triphylite chemical composition (wt. %) and unit formulae (a.p.f.u.)

Oxides (wt. %)	Samples							
	Ph-51B ¹	Ph-101B ¹	Ph-102B ¹	Ph-961 ²	Ph-962 ²	Ph-963 ²	Ph-964 ²	Ph-965 ²
SiO ₂	0,85	0,18	0,550	0,210	0,008	0,028	0,017	0,046
TiO ₂	0,00	0,003	0,00	0,005	0,00	0,028	0,00	0,00
Al ₂ O ₃	0,805	0,98	0,45	0,011	0,02	0,00	0,007	0,012
Fe ₂ O ₃	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
FeO ³	28,25	27,05	28,98	28,26	27,64	33,04	23,47	15,08
MnO	15,83	14,95	15,71	16,72	17,50	27,13	40,46	28,03
MgO	0,390	0,40	0,40	0,25	0,25	0,253	0,318	0,044
CaO	2,310	5,060	1,14	0,009	0,025	0,117	0,062	0,081
Na ₂ O	1,040	0,67	0,68	0,006	0,011	0,53	0,00	4,100
K ₂ O	0,500	0,63	0,54	0,006	0,00	0,00	0,00	0,00
P ₂ O ₅	41,98	42,25	42,13	45,17	45,21	34,76	33,58	45,06
Li ₂ O	7,560 ³	7,26 ³	8,21 ³	9,59 ⁴	9,48 ⁴	3,48 ⁴	2,76 ⁴	7,790 ⁴
ZnO	0,110	0,18	0,20	0,00	0,00	0,00	0,00	0,00
Number of ions on the basis of 4 (O,OH) (a.p.f.u.)								
Si	0,023	0,005	0,015	0,005	0,00	0,001	0,001	0,001
P	0,956	0,963	0,963	0,997	1,00	0,890	0,867	1,006
X	0,979	0,968	0,978	1,002	1,00	0,891	0,868	1,007
Ti	0,00	0,00	0,00	0,00	0,00	0,001	0,00	0,00
^{IV} Al	0,026	0,031	0,014	0,00	0,001	0,00	0,00	0,00
Fe ²⁺	0,636	0,609	0,655	0,616	0,604	0,835	0,599	0,333
Mg	0,016	0,016	0,016	0,010	0,010	0,011	0,014	0,002
Mn	0,361	0,341	0,359	0,369	0,387	0,695	1,046	0,626
Ca	0,067	0,146	0,033	0,00	0,001	0,004	0,002	0,002
Zn	0,002	0,004	0,004	0,00	0,00	0,00	0,00	0,00
Na	0,054	0,035	0,036	0,00	0,001	0,031	0,00	0,210
K	0,017	0,022	0,019	0,00	0,00	0,00	0,00	0,00
Li	0,818	0,786	0,892	1,005	0,996	0,423	0,339	0,827
A	1,997	1,990	2,028	2,00	2,00	2,00	2,00	2,00

¹ - FeO as total iron; ² - XRF; ³ - EMPA; ⁴ - ICP-MS; ⁵ - stoichiometrically determined; (Ph-51B) - lithiophilite – triphylite associated with spodumene, albite and greenish muscovite, in LPs; (Ph-101B) - (Ph-102B) - lithiophilite – triphylite associated with spodumene, quartz, albite and greenish muscovite, in LPs; (Ph-961) - (Ph-965) - lithiophilite – triphylite associated with spodumene, quartz and apatite, in LPs.

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NI-CO-BI ORE DEPOSIT FROM V. BADEANCA, LEAOTA MTS

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We investigate the metallogeny and mineralogy of some occurrences of a pentametallic ore deposit situated in the southern part of the Leaota Mts. (at the limit between Southern and Eastern Carpathians, between V. Ialomita and V. Dambovita). A broad range of ores from different paragenesis characterizes this part of the massif and mainly V. Badeanca (the main valley dominating the south of Leaota Mts.) and V. Negulet. The variety of these ores is such that almost all mineralogical and geochemical types of ores have been identified. In the present study we focus on occurrences of ores from the Ni-Co-Bi paragenesis.

These Ni-Co-Bi occurrences belong to the pentametallic ores, which represent a relatively unique genre with just a few locations in the world known to-date, each with its own peculiarities (Stanton, 1972). Their presence is intriguing and several questions related to their genesis still persist – e.g. their origin might be related to hydrothermal activity from plutonic intrusions or to mantle fluids (Halls and Stumpfl, 1972).

In the Leaota Mts. these ores have been cited scattered on some of the main valleys adjacent to V. Badeanca (V.Danis, V.Grui, V.Tancava, left side of V.Badeanca, prior to V.Mihai). The occurrences in outcrops or in various mining exploration works are scarce and have been almost completely mined out during the last decades, without finding any economic concentrations. The main minerals of these deposits are the Ni, Co and Bi sulphides and arsenides. Their mineralogy has been described based on their main cations (Petrulian, 1932, Popescu, 1968) or on deposit occurrence using several associations (Udubasa, 1993).

Based on the previous studies and on new observations (optical studies, microprobe chemical analysis) we separate three main paragenesis, which we find characteristic to the pentametallic deposits of Leaota Mts.: the safflorite $[(Co,Ni,Fe)As_2]$ – native bismuth (Bi) – bismuthinite (Bi_2S_3) – Bi sulfosalts paragenesis; the maucherite $(Ni_{11}As_8)$ – gersdorffite $(NiAsS)$ – nicheline $(NiAs)$ – millerite (NiS) paragenesis; and the safflorite – skutterudite $[(Co,Ni,Fe)As_3]$ – glaucodot $[(Co,Fe)AsS]$ paragenesis. In the following we detail the first of these paragenesis, where new mineral occurrences (Bi sulfosalts) for Leaota have been identified.

The safflorite – native bismuth – bismuthinite – Bi sulfosalts paragenesis is associated with a Ti-bearing quartz- and carbonate- gangue, where the quartz is partially corroded by the carbonate. Replacements of the host rock by silica, carbonates and zeolites are common.

Calcite is recrystallized and one can see the overgrowths of calcite towards the former void spaces filled with zeolites. Optical determinations on the zeolites show the existence of thomsonite ($R=1.49\pm1.54$). Cathodoluminescence studies and microprobe chemical analysis on the carbonate hosting the mineralization showed it to be of calcite-dolomite type, free of Mn, rich in Ca and Mg and poor in Fe (below 15%).

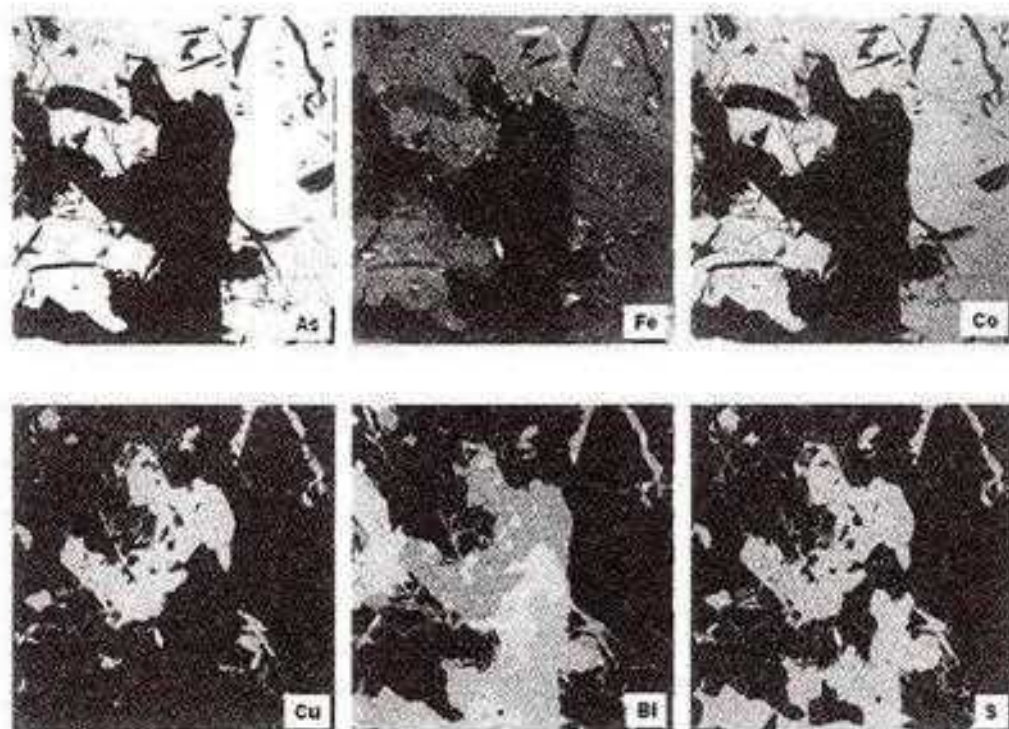
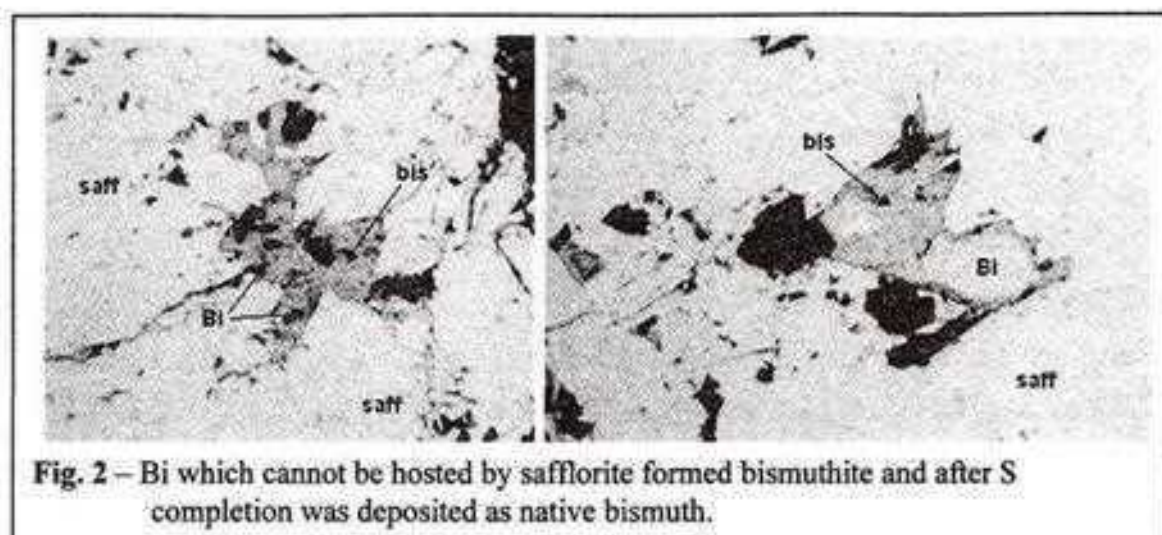


Fig. 1 – The distribution of main elements in the safflorite – native bismuth – bismuthinite – Bi sulfosalts paragenesis as shown by backscattered electrons imaging

Amongst the opaque minerals, safflorite is the most abundant in this paragenesis with euhedral and subhedral aggregates. Safflorite shows a network of intergranular cracks where carbonate, native bismuth and bismuthinite are developed. Chemically the safflorite is rich in Co, with variable Ni and Fe contents, with formulas in the $(\text{Co}_{0.47-0.52}\text{Ni}_{0.36-0.20}\text{Fe}_{0.18-0.26})\text{As}_2$ or $(\text{Co}_{0.76-0.89}\text{Ni}_{<0.01}\text{Fe}_{0.09-0.17})\text{As}_2$ range.

The native bismuth is associated with bismuthinite as inclusions in safflorite. The bismuthinite is frequently found around the native bismuth crystals or it develops as small veins in the intragranular fissures in safflorite. The chemical composition of the bismuthinite is close to the nominal values with small amounts of impurities (mainly As, Co, Fe, Cu).

The bismuthinite is mainly associated to the Bi sulphosalts, as revealed by the chemical analysis. The size of the bismuthinite crystals is often at the limit of the optical detection. Fig. 1 shows the image of the element (Co, As, Fe, Bi, S, Cu) distribution in



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TRACE ELEMENTS IN TRANSYLVANIAN GOLD NUGGETS

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The concentration values of minor and trace elements in natural gold from different regions of the terrestrial globe can facilitate gold artefact provenance studies, especially of the ancient objects, and can help to define the genesis of the gold sediments. For the Romanian history the provenance studies of very old Romanian gold hoards (such as Moigrad, gold idols found in Călărași county) would be most desirable, but the provenance of gold will also be useful for newer artifacts such as the Hinova hoard (12th century BC), the Dacian ΚΟΣΩΝ gold coins (1st century BC), or even for the Roman gold coins struck after the conquest of Dacia.

According to Pernicka (1986) the most promising elements for Au provenance determination are Ag, Cu, Te, Sn and the Platinum Group Elements (PGE). However, our opinion is that other elements, such as Hg and Pb might be valuable indicators for gold provenance studies.

Few years ago we obtained 15 nuggets from the Gold Museum in Brad. Since then a series of analyses using nuclear techniques were performed on them, such as Instrumental and Radiochemical Neutron Activation Analyses (I & R NAA), Proton Activation Analysis (PAA), and Synchrotron Radiation X-Ray Fluorescence (SR-XRF), in order to determine the composition of these nuggets from different Transylvanian mines and placers.

By INAA the minor and trace element concentrations of Ag, Cu, Ir, Pt, Hg, Al, Eu and V at trace level were determined. The sensitivity for Cu of the INAA is not very good (the detection limit is around 200 - 300 mg·kg⁻¹) and this fact made that sometimes only the upper limit of Cu concentration to be found. Concerning PGE, only Ir and Os were determined by INAA (detection limit for Ir is about 0.4 ppm); chemical separation was necessary for Pt determination. Furthermore, INAA is not sensitive enough for Te and Sn analysis. Pt was put in evidence by NAA only after chemical separation (Cojocaru & Spiridon, 1985) and only if its concentration was higher than 100 ppm.

In PAA each sample was irradiated with a proton beam of energy $E_p = 11$ MeV and a current $I_p \approx 0.3$ μ A for about 90 min at the NIPNE-HH Tandem accelerator. At this proton energy only (p,n) channel is open, so that one expects to see reactions of type ${}^Z_X(p,n) {}^{Z+1}_Y$. After irradiation and a cooling time between 24 and 48 hours, each sample was measured with

a γ spectrometer with a 50 cm² Ge(Li) detector with 2.1 keV resolution for 1.332 MeV (⁶⁰Co). A cadmium filter of 1 mm thick was used for the first counting in order to reduce very strong Au-X rays and γ -lines of 77.35 keV (¹⁹⁷Hg) and 134 keV (^{197m}Hg). The subsequent γ -ray spectrometry measurements were made without any filter. A γ -ray spectrum of a nugget is shown in Figure 1. The following elements were analysed by PAA: Ag, As, Cr, Cu, Fe, Hg, Pb, Pt, Sb, Sn, Sr, Te, Ti, Zr, Y.

PAA results are given in Table 1. The first two nuggets belong to placer deposits and the rest to primary deposits. In comparison with NAA, where parts of the nuggets were used, these results show some differences that are accounted as a lack of homogeneity. For instance, Ag shows high inhomogeneities for crystallized nuggets (the last three ones), but also for Musariu-Brad nugget. The concentrations of the rest are in agreement within the limits of ± 30 %.

Due to the larger analysed masses (for NAA, the average weight of the analysed sample was 4 mg, while for PAA a mass of about ten times larger was irradiated), PAA results are considered as being more reliable.

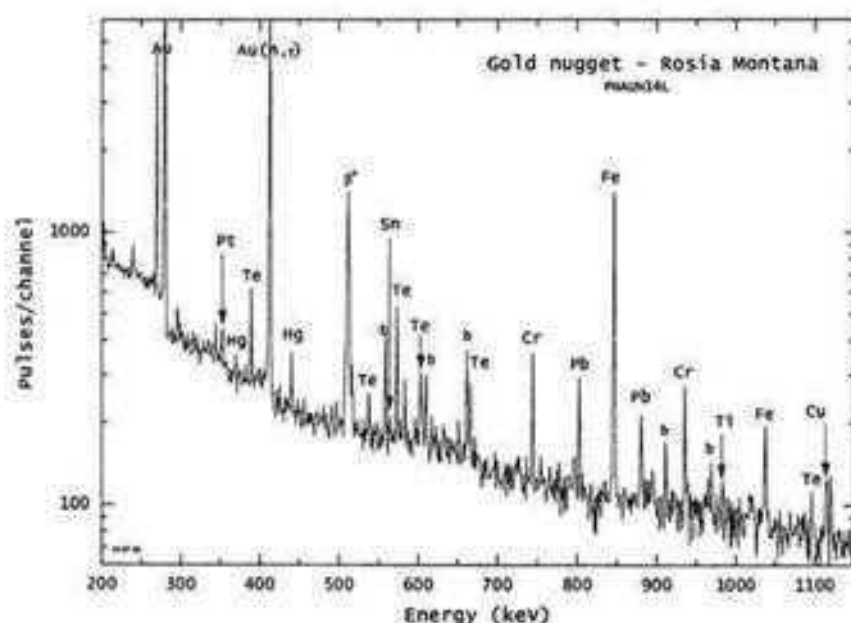


Figure 1 - Part of the γ spectrum of a primary gold nugget. Cooling time: 6 d. The target elements are marked on the graph (b = background)

The primary and placer Transylvanian gold are characterized by the following average concentrations: Ag: 15.5%, As: 53 mg·kg⁻¹, Cu: 185 mg·kg⁻¹, Fe: 630 mg·kg⁻¹, Ir $\leq$

0.4 mg·kg⁻¹ (except 2 nuggets with 0.4-0.6 mg·kg⁻¹), Hg: 400 mg·kg⁻¹, Pb: 153 mg·kg⁻¹, Sb: 82 mg·kg⁻¹, Ti: 36 mg·kg⁻¹, Te: 300 mg·kg⁻¹.

Table 1. Element concentration in gold nuggets obtained by PAA technique. The values are in ppm (mg·kg⁻¹) if no other indication is given

Source	Ag	As	Cr	Cu	Fe	Hg	Pb	Pt	Sb	Te	Ti	Zr
Valea Ariesului	6.95%	110	n.d.	540	1600	990	170	n.d.	≤13	33	335	87
Valea Pianului	12.45 %	20	n.d.	150	120	390	≤20	153	79	n.d.	11.6	1.2
Bucium-Izbita	13.95 %	55	n.d.	510	110	110	180	n.d.	≤4	≤15	0.6	2
Baia de Aries	10.20 %	14	n.d.	30	40	280	80	n.d.	3	≤10	1.8	1.6
Zlatna	27.04 %	≤18	n.d.	50	1500	230	58	n.d.	145	≤80	2.6	1.3
Ruda-Brad	13.24 %	1.46 %	5.3	220	2700	950	340	262	560	35	49	n.d.
Valea Morii	18.69 %	≤12	1	60	260	180	115	56	41	≤8	9.3	1
Musariu-Brad (1)	22.46 %	≤10	n.d.	40	60	220	122	n.d.	32	40	0.6	n.d.
Musariu-Brad (2)	4.90%	28	n.d.	340	6	100	150	58	≤5	3040	≤0.8	0.4
Runculet-Straja	22.50 %	93	n.d.	60	980	700	125	n.d.	44	300	18	≤0.6
Rosia Montană	25.65 %	≤25	4.6	25	180	200	450	n.d.	61	180	1.6	n.d.
Brădisor-Brad	8.50%	≤17	n.d.	200	13	500	36	n.d.	≤6	230	3.7	≤0.4

There is a small probability that minor and trace elements from native gold could indicate the mine from which gold has come. For example, two nuggets originating in the same mine (Musariu-Brad 1 and 2), but coming from different places, drastically differ in elemental composition, an order of magnitude or more differences in concentrations being observed. However, some average concentrations might characterize gold from a geographical region. There are only few data in literature one can compare with the Romanian native gold analyses. Nevertheless it is for sure that Carpathian gold has as fingerprint low concentrations of Cu, Ir and Sn and relatively high concentrations of Ag, Hg and Te. The last element has even been discovered by F.J. Müller von Reichenstein in Romania at Săcărâmb in 1782 and it is considered that "only in the ore deposits from Transylvania are found minerals in which tellurium is combined with gold or silver" (Chesu, 1983). Also, Ir and Os (generally PGE) seems to be different in Romanian gold. For instance, the Pietroasa hoard was

manufactured of gold in which Ir is as a solid solution (but iridosmium inclusions also co-exist) in an average concentration of 7.8 ppm (Cojocaru et al., 1999), very high in comparison with the Romanian native gold (≤ 0.4 ppm). The concentration of Ir was established to have the value of only 0.04 ppm, for a nugget investigated by radiochemical neutron activation analysis (Cojocaru et al., 1999).

In the frame of an international team - E. Pernicka, M. Radtke, A. Schmiderer and B. Constantinescu - in March 2006 several small fragments of natural (placer and primary) Carpathian (Transylvanian) gold - were studied using SR-XRF at BESSY (Berlin Synchrotron Radiation facility). The goal of the study was to identify the main trace elements for Apuseni Mountains' gold, especially Sn, Sb and Te. The measurements were performed in air by using a 34 keV beam to excite the characteristic X-lines in Sn-Sb-Te region and to relatively minimize the Au X-rays contribution. Preliminary results indicated that for the Transylvanian natural gold, Sn was found in placers from Valea Arieşului and Valea Pianului, Sb was found in primary gold from Zlatna, Ruda-Brad, Valea Morii, Runculeţ-Straja, Te was found in primary gold from Bradişor-Brad, Zlatna, Runculeţ-Straja, Valea Morii, Muşariu-Brad, Pb was present in primary gold from Valea Morii. All these results are consistent with the geological data for Brad - Zlatna region from Apuseni Mountains. These preliminary results demonstrated the important potential of SR- XRF to detect trace elements in gold to be used as provenance fingerprints.

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The mineral world includes in present about 4000 valid mineral species of various composition (from native elements to organic compounds) and size. Some 400 or 500 of the existing mineral species are known only as inclusions in other minerals and their investigation by different and adequate physical and chemical techniques reveals the chemical evolution of the minerals for metamorphic deposits. Depending on their size, such minerals can be classified as follows: (1) micro-minerals, from one millimeter down to 5-10 micrometer in size, which can be identified under the optical microscope; (2) "infra-minerals", i.e. submicroscopic inclusions, some several micrometers to thousands of nanometers in size; commonly these minerals can be identified by using EMPA; (3) "nano-minerals", of

nanometer size. The

adequate physical techniques for the growing and the presence of such nanometer inclusions are electron

microscopy (ME: TEM, SEM, SAED, HRTEM etc.) and nuclear gamma resonance (NGR, for Fe, Sn, Au, Eu, etc. species). The aim of this article is to point out the presence of

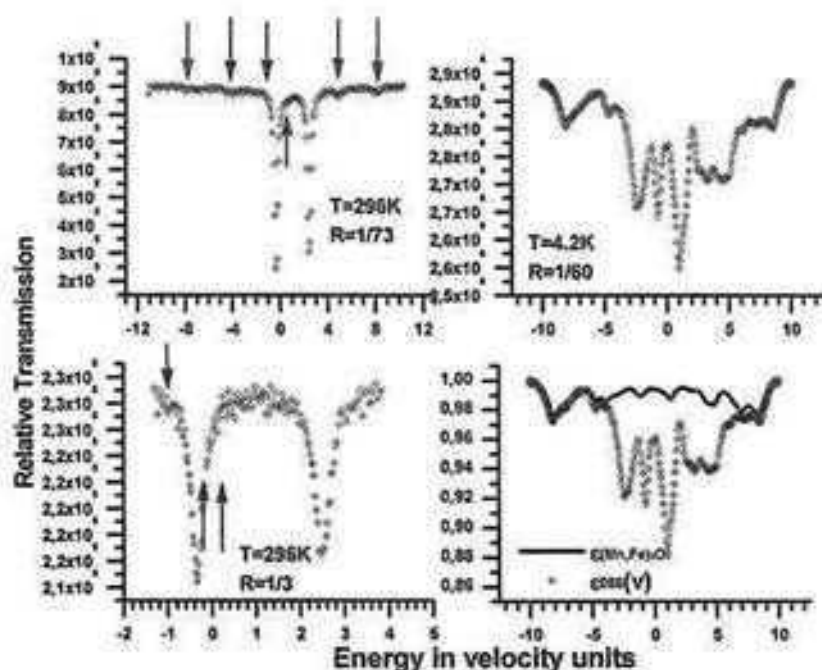


Fig. 1. The evidence of Mn-Fe oxide patterns contribution to the RT and LHeT manganoo-fayalite spectra.

nanometer inclusions in some minerals of interest, using NGR techniques and ME. The minerals of interest are extracted from the Mn-Fe Razoare deposit and gold-ores of Valea lui

Stan, Costesti and Jidostita. The NGR analysis of some Razoare manganoan fayalite (Fig. 1) reveals the presence of low intensity sextet pattern, corresponding to the small concentration of the Mn-Fe oxide in magnetic phases (down arrows).

Moreover, the evidencing distortion (up arrows) of the doublet patterns (for high-resolution spectra, $R=\Gamma_{obs}/\delta E$), one suggests the superparamagnetic state of oxides, at RT spectra. The LHeT spectra of the same samples are showing many sextet-patterns and in

Tab. 1. NGR spectral parameters of Mn-Fe oxide extract from a Razoare manganoan fayalite spectrum.

Mn-Fe OXIDE PATTERN of 088 sample	δ_{Fe} [mm/s]	$eQV_{zz}/2$ [mm/s]	B_{loc} [T]	Relative area [%]
RT				
III ¹	0.17(5)	0.60(9)	-	2.3(1)
3 ²	0.00(3)	-0.18(6)	49.0(1)	6.2(2.0)
4 ²	0.56(6)	1.04(12)	46.6(4)	8.0(2.0)
LHeT				
C	0.20(7)	-0.15(14)	52.0(5)	15.7(2.8)
D	0.90(7)	-2.13(14)	45.1(5)	14.6(2.8)
E	1.40(10)	-1.27(19)	43.7(5)	5.1(4.2)

consequence an apparently growing of magnetic phase weight, see the Table 1,

(Constantinescu 2001, 2003, for details). The RT distortion of the spectrum central doublet and the apparently growing

of the magnetic phase at LHeT have suggested the presence of the Mn-Fe oxide in small particles (under $\sim 150\text{\AA}$) on the surface and/or inside of manganoan fayalite grains. In deed, the growing of the sextet patterns with the temperature decreasing corresponds to the increasing both of the volume energy vs. thermal one ratio, and of the magnetic local field's time flipping at the ^{57}Fe Mössbauer probe.

On the other hand, TEM analysis of Razoare manganoan-fayalite has revealed the presence of pyroxferroite crystals and the wustite, mangano-grunerite (formerly dannemorite) and magnetite nano-precipitations (Constantinescu et al., 2004, Fig. 2). The identification of wustite (as precipitation and/or microinclusions) and pyroxferroite (as single crystals with perfect geometrical shape) in the manganoan fayalite gives a deeper insight into metamorphic evolution of the Razoare Mn-Fe deposits, the largest of this kind in Romania, with a geological age of more than 550My. The PT estimations, based on the mineral assemblages, shows highest metamorphic peak to slightly exceed the upper amphibolite metamorphic facies (about 700°C and 700MPa) entering the field of eclogite facies. After primarily crystallization of manganoan orthoferrosilite, the manganoan fayalite has formed on it, being the first retrograde transformation; the second retrograde transformation was that of manganoan fayalite into mangangrunerite. Udubasa et. al. (1996) supposed that the second retrograde

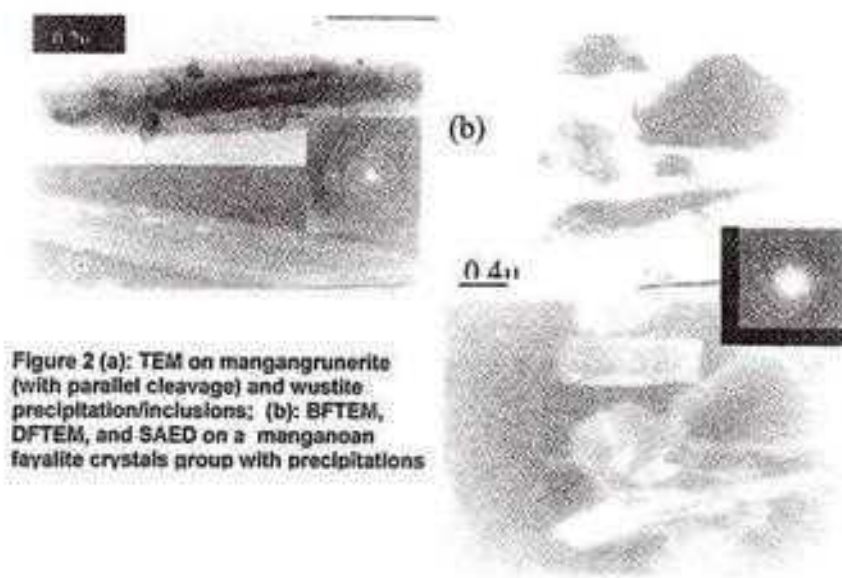


Figure 2 (a): TEM on mangangrunerite (with parallel cleavage) and wustite precipitation/inclusions; (b): BFTEM, DFTEM, and SAED on a manganoan fayalite crystals group with precipitations

transformation of manganoan fayalite includes mainly mangano-grunerite (formerly dannemorite). It is to note that abundant mangangrunerite is accompanied by development of magnetite by increasing oxygen fugacity during the late

evolution of the deposit.

The recent analyses have evidenced both "infra-minerals" and "nano-minerals" in the gold ores of Valea lui Stan, Costesti and Jidostita, containing pyrite, arsenopyrite, chalcopyrite and pyrrhotite as major minerals (see Udubasa S.S., 2004 and Udubasa S.S., 2006 for details). So, the TEM/SAED analyses carried out on powder samples from Costesti and Valea lui Stan sulfides, have evidenced nanometric "precipitates" of Au or Au-Ag alloy on pyrite or pyrrhotite grain surfaces. Those are showing diverse morphologies, i.e. from isolated nano-particles, some tens of nanometers in size, up to "coral-like" aggregates (Fig. 3).

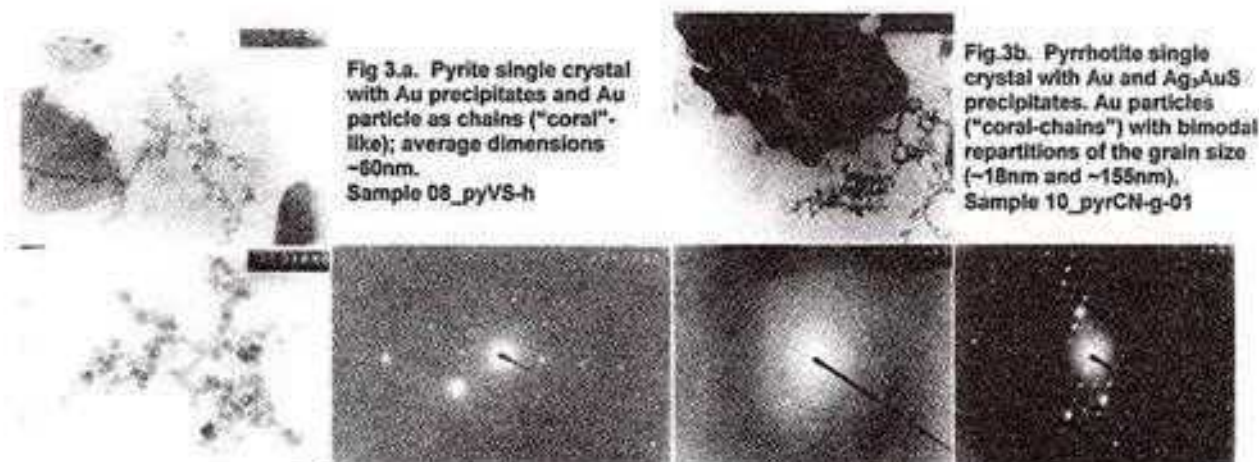


Fig 3.a. Pyrite single crystal with Au precipitates and Au particles as chains ("coral-like"); average dimensions ~60nm. Sample 08_pyVS-h

Fig.3b. Pyrrhotite single crystal with Au and Ag-AuS precipitates ("coral-chains") with bimodal repartitions of the grain size (~18nm and ~155nm). Sample 10_pyrCN-g-01

Such nano-grains or aggregates have also been identified (although more rarely) on arsenopyrite and chalcopyrite. Usually these aggregates or precipitates are observed ("built") at edges or/and corners of the crystals.

Instead of conclusion one remarks the capability of combined investigation techniques (EMPA, ME, NGR) to evidence the third level of the inclusions at nano-size scale. This level, which could appear during the metamorphic processes, has been predicted in Udubasa (2004, 2006). The analyses and interpretation of the NGR, ME data are in progress in order to

elucidate the role of the mechano-thermo-chemically processes supported by the above mentioned mineral deposits on the gold trap and nanosize gold inclusions/precipitates and aggregates.

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NATIVE GOLD IN THE BAIA MARE METALLOGENETIC DISTRICT

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The epithermal ore deposits of the Baia Mare district are related to Neogene volcanic rocks (Badenian – Upper Pannonian). The Neogene magmatic arc and the associated metallogenesis from the Eastern Carpathians are related to the final stage of evolution of the Tethys Ocean between Africa and Eurasia. The volcanic activity has an initial acidic character leading to a volcanoclastic complex of lower Badenian-Sarmatian age, largely developed between Racşa and Firiza Valley. Largely spread are the Sarmatian – Pontian volcanic manifestations represented by andesites. The complex of lava flows is accompanied by various intrusive bodies.

The intrusive magmatism has a subvolcanic and intravolcanic character. The spatial relationships suggest an ulterior emplacement of the intrusive bodies in relation to the lava flows (especially the Sarmatian ones). These intrusions have an essential role in the genesis of the ore deposits.

The metallogenetic phases are complex, consist of mainly base-metal, and gold mineralization, subordinately copper. They show a polyascendant character. For the gold veins and veins of small dimensions the monoascendant character is predominant. Five areas can be distinguished as resulting from: (1) the association of the ores with volcanic rocks of different ages, and (2) the prevalence of metals in the ores:

A. Turt Ghezuri ore deposit

The Ghezuri ore deposit is placed in the Oaş metallogenetic district and has a base-metal predominant character (Jude, 1986). The ore deposit is located in the western part of the microgranodiorite subvolcanic body. The native gold was identified in the first high temperature paragenesis of ilvaite, magnetite, pyrrhotite, chalcopyrite, cubanite, pyrite, having a pneumatolitic character. The native gold grains have a submilimetric size (0.058 - 0.044mm), an isometric shape and are included in ilvaite. Co-crystallisation is suggested from the mutual boundaries relationships. The native gold contains silver, copper and tellurium. The crystallisation of ilvaite took place at about 400°C suggesting a similar temperature condition for the native gold.

B. The western area (Ilba – Băița) ore veins containing mainly base-metal and copper ores and subordinately gold-silver ores.

The copper ore deposits from Nistru in the central vein area is associated to the subvolcanic porphyry quartz-monzonitic body and contain Bi-sulphosalts (bismuthinite-

aikinite series, cosalite, and lillianite–gustavite series), and native gold (Damian F., 1999). The association of the Bi-minerals with the native gold suggests their simultaneous and ulterior precipitation to the sulphides (pyrite, chalcopryrite and pyrrhotite). The native gold-Bi-minerals association is situated in the central part of the copper vein. The native gold appears as gold visible under microscope as well as “invisible” gold (Damian F., 1999). The morphology of the visible gold is dominated by the particles that are nodular and lamellar partially delimited by plane surfaces. Nodular and oval grains of gold are included in pyrite crystals and they are associated with lillianite-gustavite grains being disseminated in quartz.

The compositional data of some gold grains associated with Bi-minerals from chalcopryrite, obtained by microprobe analyses, emphasised their relatively high fineness, (Au 83.30%, Ag-15.70%). By Secondary Ion Mass Spectroscopy (SIMS) the “invisible” gold has been emphasised within the euhedral pyrite crystals. The presence of the gold (3-64ppm) and silver (1-92ppm) content in the pyrite crystals has confirmed their role of potentially important Au and Ag-carrier. The dispersion of the “invisible” gold supposes high temperatures, around 300°C. If the temperature becomes lower than this value the gold crystallises in native state and it is included in sulphides and in quartz.

The native gold occurs both in the Nistru base-metal ores, as inclusions within chalcopryrite, galena, sphalerite, pyrite and quartz. The morphology that Au adopts within sulphides is dominated by the isometric shape, minute or larger grains and rarely filaments. Small amounts of gold appear included in goethite. At Ilba about 60 percent of observed gold grains occur in quartz, having the fineness of 720. The fineness increases at Băița i.e. of 760.

In the gold-silver ore deposits the native gold is included in quartz.. The native gold may occur as inclusions within pyrite idiomorphic and xenomorphic crystals. The gold grains are intergrown with chalcopryrite. In some cases the gold occurs along boundaries between galena and sphalerite or as minute grains within pyrrhotite. The gold is locally associated with iron oxides, (goethite and lepidocrocite) in the areas affected by the supergene processes. The variety of morphologies of the gold indicates the variation of the chemical factors during the local condition of crystallisation. Grains with a medium size of 0.012mm are predominant and grains that are larger than 0.050mm are less present while the maximum size for the gold grains is 0.144mm. The gold fineness is 700. Silver is present in subordinated quantities that vary from grain to grain.

C. The central area (Săsar) with quartz-andesites of Pannonian age and Au – Ag ore veins or stock works. Gold is associated either with quartz (about 30 percent), iron oxides (5 percent), sulphides (38 percent) and carbonates. The gold in the quartz veins has nearly the

same fineness (610–763) as compared to the gold associated with pyrite in the stock works (640–730). The native gold from Săsar is frequently visible under the microscope and only rarely visible macroscopically (Dealul Crucii ore deposit).

At Borzaş, based on research carried out by Damian et al. (1996) the native gold is associated with pyrite (about 90 percent) and only a small part appears within quartz, sphalerite and galena. The grains of the native gold range between 0.008 and 0.047mm, with a medium size of 0.019mm. The larger grains of the native gold, with euhedral shape are associated with pyrite.

Within the Sofia vein group the native gold occur as euhedral grains, between 0.104 and 0.004mm in size (with a medium of 0.013mm) in sphalerite and in the fine-grained quartz matrix. At Valea Roşie, in the lower parts of the veins the native gold is associated with sphalerite and pyrite and subordinately with quartz and carbonates. Grain size is generally less than 0.240mm.

In the Aurum, Wilhelm, Adam-Cremenea vein groups, the native gold occurs almost exclusively in quartz and carbonates and was observed rarely in sulphides. Gold as small grain, between 0.096 and 0.004mm in size, forms clusters within quartz.

It is most likely that this generation of native gold is crystallized from the last solutions which contained fluids rich in meteoric waters. The fineness of gold is between 590 and 735. The low values of the Săsar native gold fineness suggest that it was crystallised at temperatures characteristic to the epithermal domain and close to the surface. The gold fineness is approximately the same in all the vein mineralizations and for the native gold from the Borzaş stock the fineness a little lower.

D. The eastern area (Baia Sprie – Băiut) with ore veins bearing both base-metal sulphides and gold.

At Baia Sprie the gold is mostly associated with sulphides (mainly pyrite, about 68 percent) and has a fineness 715 – 740 as compared with the gold in quartz (about 31 percent) of significant lower fineness (650).

The base-metal Şuor-Cremenea deposit is one of the most economically important within the Baia Mare district. Cremenea vein of Şuor has an obvious vertical zonality, the upper gold-silver bearing part gradually passing into a lower lead-zinc bearing zone with gold content. The native gold has been identified in the shape of izometric grains with euhedral forms of micrometer size and rarely appears as longer filaments.

In the upper gold-silver bearing zone, gold is mostly associated with quartz (80 percent) and less with sulphides (pyrite and sphalerite). The grain size is small, between 0.004

and 0.024mm. Gold is associated with pyrite and sphalerite within veinlets with sulphides that crosscut the bands of rubanate quartz.

In the lead-zinc bearing zone the native gold is predominantly associated with sulphides, presenting the following distribution: in pyrite 25%, in sphalerite 34%, in galena 24%, in arsenopyrite 0.5%, in tetrahedrite 0.5% and 16% in quartz. The grain size of gold in these parageneses ranges between 0.004 and 0.194mm. Both in the upper zone and in lead-zinc bearing zone, the presence of two native gold generations can be recognised. The native gold identified in pyrite and quartz is lower in size than the medium size. The estimated gold fineness varies between 730 and 785.

The ore deposits of the Băiut area represent the eastern extremity of Baia Mare metallogenetic district. The ores forming veins of base-metal character, contain gold too. The native gold appears visible only by microscope. The fineness of gold in the Băiut veins is 780-980. In the veins of Breiner Băiut group native gold is associated with pyrite 49.8%, sphalerite 36.5% and quartz 13.7%. In the Cisma-Poiana Botizei area native gold appears included only in pyrite. Three associations of the native gold can be distinguished in the Văratec-Băiut vein group:

- gold - quartz 55% and sphalerite 25% (in the eastern part);
- gold - quartz 47% and pyrite 23% (in the central part);
- gold - quartz 42% and chalcopyrite-bismuth sulphosalts 45% (in the western part).

E. The Neogene intrusion of Toroiaga-Țiganul was emplaced as a result of the multistage magmatic activity. The mineralizations are predominantly copper bearing and only partly lead-zinc bearing (Piciorul Țiganului). In most cases they consist of massive pyrite with chalcopyrite. Some of the parts veins contain also sphalerite, galena, pyrrhotite, marcasite, arsenopyrite, bismuth-minerals and other sulphosalts (Cook, 1997).

Native gold has been observed in the Domnișoara, Orania, Caterina and X veins. It appears included in sulphides and only subordonately in quartz. It occurs as isometric grains within pyrite or along grain boundaries between pyrite and quartz, chalcopyrite and sphalerite. Secondly it forms small inclusions in sphalerite and galena. Grain size is generally less than 48 microns. Gold in the Toroiaga veins show a high fineness (910 and 980).

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More than 250 valid mineral species are now known in the rocks and mineral occurrences of the Ditrău alkaline massif, from which about a quarter have been proved to contain REE and the associated Y. The Ditrău massif was supposed to contain also carbonatites (Hirtopanu et al., 2000) and it was proposed that the „official” name should be “the Ditrău carbonatite alkaline intrusive complex” (DCAIC). The DCAIC is unique in the East Carpathians; it was emplaced within the metamorphics of the Bucovinian Nappe. Field relations and measurements support a multi-phase evolution developed mainly between a Triassic extensional stage and a Jurassic rifting stage (Kräutner & Bindea, 1996). According to these authors the timing of the DCAIC is as follows: (1) a mantle derived gabbroic magma emplaced in extensional regime, carrying ultramafic mantle xenoliths, forming an outer ring (230 Ma); (2) intrusion of a crustal syenitic magma, producing foliated rocks as well as hybridization of gabbroic rocks (215 Ma); (3) a nepheline syenite intrusion (160 Ma), forming a central stock and pervasively penetrating the older rocks. A late phase with lamprophyre veins and dykes, including also the rock alteration and ore-forming processes have probably lasted until Lower Cretaceous.

The high petrographic complexity of the DCAIC showing both parental and hybrid rocks is doubled by a great diversity of mineral occurrences. About 85 mineral species have been previously described (Constantinescu, 1999; Jakab, 1998), a number significantly increased after the excellent work of Hirtopanu (2006) to about 200, of which some 50 are REE bearing. The REE and Y bearing minerals of the DCAIC belong to the following mineral classes: halides, oxides, carbonates, phosphates and silicates, representing the aim of this paper.

The halides commonly occur in albitites originating in the alkali syenites as late differentiates as well as in the hydrothermal deposits related to alaskites and nepheline syenites at Ditrău. The glimmerites resulted by fractionation of the carbonatite magma consist of phlogopite, alkali amphiboles and calcite, e.g. at Jolotca and may also contain Ce bearing fluorite, fluocerite, cryolite and probably gagarinite. At Lăzarea an yttrian fluorite was identified.

The oxides are widespread in the DCAIC and formally belong to two categories: common oxides and REE bearing (commonly complex) oxides. The common oxides occur as

accessory minerals in rocks (magnetite, hematite, chromite, rutile, etc.), in contact metamorphic rocks (corundum, spinel, hercynite, srilankite) or elsewhere (chromspinel, ilmenite, zirkelite, senaite). Ilmenite is the most frequent oxide mineral in the REE-bearing ores at Jolotca.

The complex, REE bearing oxides contain Ti and/or Ta and Nb as well as U, a fact leading to metamictization of some mineral species such as aeschynite, fergusonite, fersmite, loparite, samarskite. All of them occur as accessories in the nepheline syenites and in the carbonatites.

The columbite group is best represented in the DCAIC (but not exclusively) by ferrocolumbite, commonly zoned, with red nucleus (transmitted light) and opaque rims. Ferrocolumbite is at home in the REE bearing carbonate occurrences and in those with pyrochlore (at Aurora), sometimes in the pneumatolitic assemblages with fluorite, beryl and Li micas (at Hereba). As a rule, the columbite minerals show pervasive substitutions with pyrochlore and fersmite. Y and Ce are minor constituents of these minerals.

The pyrochlore group minerals were early recognized in the DCAIC, e.g. Anastasiu & Constantinescu (1977). However, the new defined mineral species of the group, i.e. kalipyrochlore, bariopyrochlore, plumbopyrochlore, ytropyrochlore, ceriopyrochlore and uranypyrochlore have been identified only in the last time, mostly in carbonatites as well as in glimmerites and fenites. They form mainly simultaneously with apatites. Some betafites and microlite are also likely to exist in the DCAIC.

The perovskite group minerals, i.e. perovskite, loparite and latrappite occur in lesser amounts as compared with the above mentioned complex oxides. They have been identified in the ore occurrences at Jolotca and Hereba, in assemblages containing also titanite and Ti-bearing biotite.

The carbonates of the DCAIC form also two categories, i.e. common carbonates (calcite, siderite, ankerite, dolomite, etc.) and REE carbonates, which commonly contain also fluorine and groups of complex anions such as carbonate-silicate, uranyl-carbonate and uranyl-silicate-carbonate. The REE and F bearing carbonate minerals are generally primary minerals in nepheline syenites and carbonatites; the bastnaesites, the the hydroxylbastnaesites (-Ce, -Nd), synchysites and parisites belong hitherto; there is also a generation of secondary REE carbonates, formed at the expense of apatites, monazites and allanites. Such are: parasites and synchysites as well as ancylite and lanthanites. In the DCAIC the REE carbonates contain mainly LREE and Ce.

The identification of REE carbonates has been performed with the aid of XRD and all of them have proved to contain mainly Ce. Nevertheless, optical mineralogy helped a lot in

distinguish them; cordylite is optically negative and has a higher refringence as compared with bastnaesites, synchysites and parasites. In addition, allanitization is typical of cordylites, occurring at the grain boundaries. Cordylites-rich assemblages have been identified in the outcrops of the Ditrău valley and in the waste dump materials of the Aurora deposit (up to 30%), reminding søvite-related assemblages.

The phosphates are less numerous as compared with the carbonates but they form significant concentrations, i.e. real REE ores, for example at Jolotca. Here the monazite-(Ce) forms radially disposed crystals up to 1 cm in size and is associated with pyrite, sphalerite, galena, ilmenite and ilmenorutile. In some other places, e.g. Hereba, Cianod, the monazite-(Ce) is associated with REE carbonates and REE allanites. Other phosphates occur in carbonatite-related occurrences, either as primary minerals (practically all the species of the apatite group, crandalite, xenotime, the silica phosphate cheralite) or as secondary minerals (rhabdophanes).

An important feature of many apatites from the DCAIC is the presence of inclusions, sometimes exsolution-like, of bastnaesites, parisites, monazites and allanites. In addition, the overall high phosphorus content of the DCAIC magmas, the intimate association of monazites with allanites, the dominance of the monazites-(Ce), the great frequency of the REE bearing minerals in general seem to strongly support the idea of the carbonatites presence in the Ditrău massif.

The silicates containing Nb, Ta, Ti, Zr and REE are widely distributed in the Ditrău rocks and their presence is a supplementary argument in designating this massif as carbonatite-alkaline, formed under anrogenic conditions. The Nb:Ta ratio, largely supraunitary, further supports the idea.

The allanite-(Ce) is the most widespread silicate and occurs in metasomatites, in association with fluorite, fluorapatite, parisites, pyrochlores and monazites. Crystals of allanite of prismatic habit with sizes exceeding 1 cm were frequently found in different occurrences.

The following Nb-Ta bearing silicates, some of them containing also Ti, Zr, Sr and REE were also identified: astrophyllite, baratovite, catapleiite, eudyalite, fersmanite, götzenite, hiortdahlite, kupletskite, lavenite, lovozerite (?), melanocerite-(Ce), rosenbuschite, thorite, titanite, wöhlerite, yttrialite, zircon, etc. Following a very detailed optical investigation on hundreds of samples covering the whole area of the DCAIC most of the mineral species were analysed by XRD and SEM. Further species are expected to occur, all of them compatible with the status of Ditrău as a carbonatite-alkaline complex.

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CL SIGNATURE OF DIAMONDS FROM UHP ROCKS OF THE KOKCHETAV MASSIF, KAZAKHSTAN

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The main purpose of this study is to investigate some diamond-bearing gneisses and garnet-pyroxene-quartz rocks from the Kokchetav Massif for the SEM-CL signature of diamonds. The Kokchetav Massif of northern Kazakhstan is the type-example of diamond-eclogite facies metamorphism. The petrographic studies made in the last years have proved that the diamond-bearing rocks have been subducted into the mantle at depths greater than 120 km.

The SEM used in this study was a Cambridge Stereoscan mod. 360 equipped with an Oxford MONO-CL system at the University of Turin, Italy.

In the Kokchetav Massif, microdiamonds are common inclusions in garnet, zircon, and rarer in clinopyroxene, kyanite, zoisite, quartz, biotite, and phlogopite from garnet-biotite gneiss, garnet-biotite-clinozoisite gneiss, garnet-kyanite-phengite-quartz schist, garnet-pyroxene-quartz rock and dolomitic marble (Sobolev & Shatsky, 1987, 1990; Shatsky *et al.*, 1995; Zhang *et al.*, 1997; Katayama *et al.*, 2000, 2002; Ogasawara *et al.*, 2000; Korsakov *et al.*, 2002).

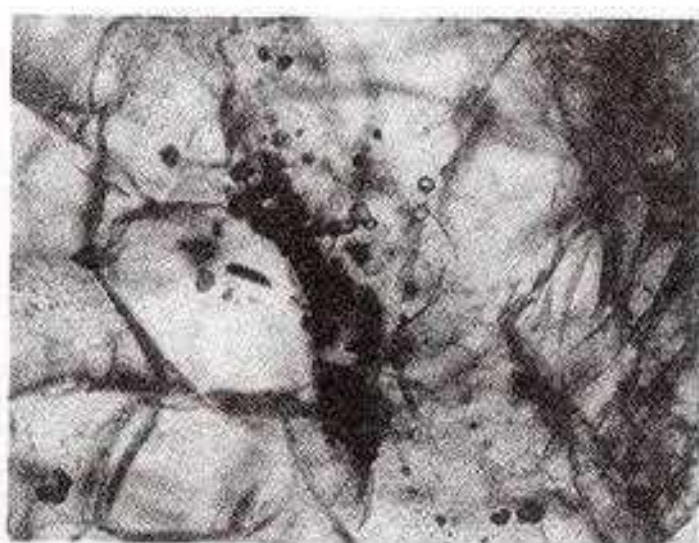


Fig. 1. Diamonds included in garnet from garnet-biotite-clinozoisite gneiss, PPL. Scale bar is 100 μ m

Microdiamonds are also commonly found in the pseudomorphs after garnet, consisting of mica + chlorite + amphibole aggregates $\pm$ tourmaline (Sobolev & Shatsky, 1990; Shatsky *et al.*, 1995). Diamonds were rarely detected as intergranular phase in quartz–feldspar (Qtz–Kfs) aggregates (Korsakov *et al.*, 2004). As usual, diamonds coexist with graphite. In dolomitic marbles, graphite is included in dolomite and occurs either as polycrystalline aggregate (5–30 μm) of extremely fine-grained crystals or as euhedral crystals with platy habit (20 μm x 75 μm); the former graphite aggregate may be pseudomorphous after diamond (Ogasawara *et al.*, 2000).

Cathodoluminescence (CL) spectral measurements of the diamonds from dolomitic marbles and Grt-Bi-gneisses, made at Room Temperature (RT), revealed emission bands and peaks in the electromagnetic spectrum between 2.01 eV (617 nm) and 3.16 eV (392 nm).

Some spectral features may be considered a possible signature of Kokchetav diamonds: 2.15 eV, 2.38 eV, 2.40 eV and 2.84 eV. In particular, the peak at 2.38 eV (521 nm – in the green part of the spectrum) is present in all the diamonds studied and has the highest intensity (see figure). The 2.47 eV center, commonly observed in some virgin good quality CVD diamond films or in boron-doped CVD diamond films, is attributed to a boron-related defect (Heiderhoff & Balk, 1995).

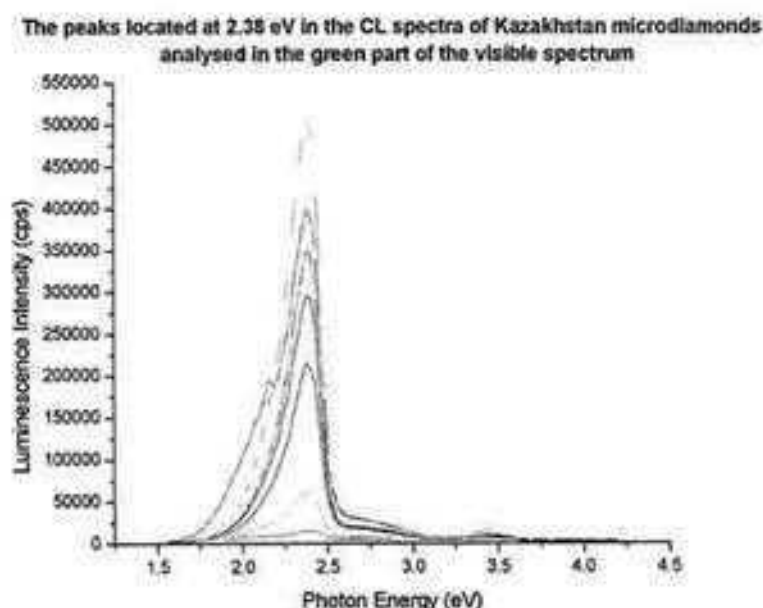


Fig. 2 The peaks located at 2.38 eV in the CL spectra of Kazakhstan microdiamonds

According to Zaitsev (2001), the peaks located at 2.84 eV and 2.99 (really 2.985) eV are due to the N3 center, the last one being interpreted as a Zero Phonon Line – ZPL. The N3 center, i.e. N₃V (three N atoms and a vacancy), is a very common feature in most type Ia

natural diamonds containing the B-centers of nitrogen. About 95% of natural diamonds reveal N3 center luminescence belonging to the type Ia (Yelissev, 1977 fide Zaitsev, 2001). The N3 center may be highly localized at cracks or regions of plastic deformation (Kanda & Watanabe, 1999). Some transformation of the B-aggregates of nitrogen into the N3 center in natural type IaB diamonds occurs at temperatures above 1960°C. No formation of the N3 center at high temperatures occurs in type IaA diamonds whereas it is formed in type Ia+Ib diamonds (Brozel et al., 1978).

False RGB colour images of diamonds, analysed by monochromatic CL, reveal zones with different luminescence, which may be due to different nitrogen contents. The images suggest that the internal "growth sectors" with different nitrogen concentrations (core rich in N_{tot} and rim with a high degree of nitrogen aggregation) are distinct zones typical either of cubes with concentric zonal structure, octahedrons with layer-by-layer 'closed' octahedral zoning, or dodecahedroids with rounded zoning (Kaminsky & Khachatryan, 2004). In our opinion, the nucleation of diamond crystals was not simultaneous, but occurred during several growth stages over a significant time interval.

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NEOGENE VOLCANISM RELATED ARSENIC SULPHIDE PARAGENESIS FROM LĂZĂRESTI AND BODOC (CIOMADU AREA, HARGHITA MTS.), AND COVASNA

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Introduction

In the Ciomadu area of the Harghita Mts. and adjacent areas, as Covasna (Covasna-Bai) a strong post-volcanic activity is present, mainly developed as solfataras and mineral waters springs. The presence of minerals related to this post-volcanic activity, like native sulphur, gypsum and related sulfates (from solfataras), or realgar together with aragonite (from water spring deposits) was early reported by Hauer (1860) from Covasna. In the surrounding areas at least two more arsenic sulfide bearing occurrences has been revealed, at Lazaresti, on the northern part of Ciomadu (Szakáll et.al., 2006) and at Bodoc (in the present study). In most of the occurrences different carbonates (calcite, aragonite, or dawsonite – for this last Covasna is the first occurrence in Romania, by Papucs, 2000) accompany the arsenic sulphides.

The presence of realgar and orpiment is an usual phenomenon in most of the Neogene hydrothermal ore deposits from the Carpathian region. Alacranite, however, is a more rarely occurring form of arsenic sulphide, with only a few occurrences known worldwide (Szakáll et. al., 2006), the Lazaresti occurrence being the 2nd for the Carpathians.

The present study is an inspection of the three known occurrences of arsenic sulphide associations from the Ciomadu area, in the light of recent results and references.

Materials and methodes

The analysed samples were collected on several occasions, recently from the occurrences at Lazaresti and Covasna and from museum samples for Covasna (Herman Ottó Museum, Miskolc and Mineralogical Museum of the Eötvös Loránd University, Budapest, Hungary) and Bodoc (Seklers National Museum, Sfântu Gheorghe, Romania). A brief description of the samples for the three occurrences is given in Table 1.

For X-ray Powder Diffraction analysis, performed at the Department of Mineralogy and Petrology, University of Miskolc (Bruker D8 Advance diffractometer), a careful single-

grain separation under optical microscope was necessary in order to obtain the most possible homogeneity of the samples. Due to small amount of material, in most of the cases a special method of sample preparation was adopted, namely, after grounding the sample to the desired size in an agate mortar, a suspension was obtained by adding a small amount of 95% etilic alcohol. This suspension was then applied on a “zero-background” sampleholder, and after drying the XRPD pattern for the “pure” sample was collected.

Due to the sample height error some displacement of the patterns occurred, which were resolved by the pseudo-Voigt fitting algorithm full pattern matching (FPM) operation of the EVA-Diffracplus software.

Single crystal X-ray diffraction (SCXRD) analyses for samples from Lazaresti were performed at the Department of Earth Sciences, University of Firenze on CAD4-Enraf Nonius and Oxford Xcalibur™ 2 diffractometers. Whenever the phase revealed to be a single crystal, the unit-cell parameters were determined routinely. However, most of grains, although minute, gave a polycrystalline pattern. In such cases a rotation photograph was done and *d* values were averaged on several points for each diffraction ring.

Table 1: Description of samples

Occurrence	Lazaresti	Covasna	Bodoc
Occuring form, Hosting rock	as matrix of sandstone, euhedral crystals in cavities	as veins and masses in spring-deposited carbonates in sandstones	as earthy masses in veins of sandstones
Sample name	G179: small orange grains (mixture)	G178	G222: mixture
	LF_2_1a: euhedral light orange prisms	G180	Bod_1: orange-yellowish mass of grained material
	LF_2_1b: euhedral dark orange-red prisms	G183	
	LF_2_1c: yellow grains	G184	
	LF_2_2: light yellow earthy crust		
Associated with	rock-forming quartz, muscovite, feldspar	aragonite and calcite	aragonite

The XRPD and SCXRD investigations were completed with Scanning Electron Microscopy (SEM) observations combined with Energy Dispersive Spectrometry (EDS).

Results

By the XRPD investigations for samples of the Lazaresti occurrence alacranite (As_8S_9), realgar (As_4S_4), orpiment (As_2S_3) and an unnamed arsenic sulphide ($\text{As:S} \sim 1:1$, approximately) were identified. The results of XRPD for alacranite are listed in Table 2. For

sample LF_2_1c the XRPD show significant match to the #048-1247 PDF card, monoclinic AsS (Douglass *et.al*, 1992), but the single crystal diffraction gave only a few lines at 4.85; 3.59; 2.88; (broad band at 2.53-2.48) Å. In the sample LF_2_2, light yellow earthy crust on altered surface, orpiment was identified.

Sample	#042-0537 (N)		G179		LF_2_1a	
Lines	d (Å)	I%	d (Å)	I%	d (Å)	I%
(3 1 0)	3.064	100	3.063	89	3.062	100
(-1 1 1)	5.910	90	5.874	77	5.873	92
(-2 2 2)	2.950	90	2.934	100	2.934	92
(1 1 1)	5.110	80	5.096	68	5.096	81
(-1 1 2)	4.050	70	o.l.		4.021	70
(0 2 2)	3.291	50	o.l.		o.l.	
(1 1 0)	6.890	40	6.867	33	6.868	40
(0 2 0)	4.870	30	4.858	24	4.867	30
(-2 2 1)	3.380	30	o.l.		o.l.	
(-3 2 1)	2.707	30	2.704	24	2.705	29
R/R0			1.32		5.61	
R _w (%)			41.6		28.3	

fitting, R=R_w, R0 discrepancy)

Table 2. Results of XRPD investigations and fitting report for the alacranite samples. The intensities (I%) have different degrees of deviation from the PDF file (#042-0537) due to measuring method. Overlapping (o.l.) by associated phases also occurs.

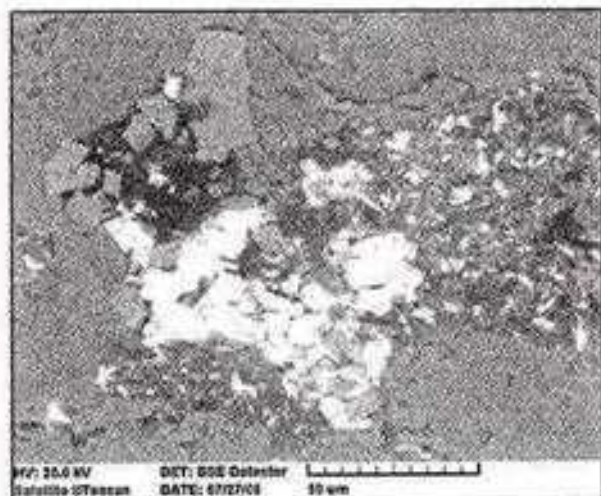
(R_w weighted reliability of FPM

By SCXRD high diffraction-quality single crystals (orange-red in color, LF_2_1b) were found to be realgar, with unit-cell parameters closely matching those reported in literature (Mullen and Nowacki, 1972). For few single crystals (light orange in color, LF_2_1a) showing a relatively poorer diffraction quality the unit-cell parameters were those of the mineral alacranite (Popova *et al.* 1986), within the experimental errors. For grains (light orange, LF_2_1a) showing a polycrystalline behavior the *d* values averaged on several each diffraction ring matched fairly well the diffraction pattern of alacranite. Refinement of the unit-cell led to the following values: $a = 9.91(1)$, $b = 9.64(2)$, $c = 9.176(9)$ Å, $\beta = 101.93(8)^\circ$; $V = 858$ Å³; $a = 9.87(1)$, $b = 9.72(3)$, $c = 9.181(8)$ Å, $\beta = 101.4(1)^\circ$, $V = 863$ Å³; $a = 9.872(4)$, $b = 9.676(3)$, $c = 9.133(8)$, $\beta = 102.5(1)^\circ$, $V = 851$ Å³. The scattering of the values is likely due to the scarce precision of the method.

A good diffraction-quality single crystal (deep orange in color) gave the following parameters: $a = 9.967(8)$, $b = 9.355(7)$, $c = 8.944(9)$, $\beta = 102.37(8)$, $V = 814.6(1)$. Using the linear equation $V = 801(2) + 1.04(5) [\% \text{As}_4\text{S}_5] (\text{Å}^3)$ ($r = 0.989$) published by Bonazzi *et al.* 2003 (*Eur. J. Mineral.* **15**, 283-288) we can tentatively estimate the following formula: As₃S_{8.26} (= 13 % As₄S₅). According to recent finding (Bonazzi *et al.* 2006), non-stoichiometric As₄S_{4+x} sulphide could form by light-induced alteration on β-As₄S₄ phase, the high-temperature polymorph of the tetra-arsenic tetra-sulfide. A grain (deep yellow in color)

exhibited d values closely matching the diffraction pattern of pararealgar, As_4S_4 (Roberts et al. 1980). These phases were not found by XRPD analysis.

The samples from Covasna taken in analysis are of realgar associated with calcite and aragonite. In sample G180 from Covasna pharmacolite was identified, but seemingly it has formed during oxidation of the exposed sample. For the sample Bod_1 from Bodoc the XRPD results showed the presence of arsenolite, the As_4S_4 mineral (#053-0529 (I),



Gospodinov, 2001) and an iron bearing (according to EDS results) rhodocrosite (Fig. 2). Single crystal diffraction was not performed on arsenic sulphide, since the crystal size is too small to select single crystals.

Fig.2 SEM image of a Bodoc sample. Note the dark rhombohedra of carbonate, light octahedra of arsenolite and small grains of arsenic sulphide, in the crack of an aragonite prism!

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PREHNITE, NATROLITE AND ANALCIME IN THE METABASITES
FROM VÂRGHIS (ROMANIA)

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In the Persani Mts. an ultramafic magmatite series of Mesozoic (Triassic) age is developed, mainly as allohtoneous ophiolite klipps. Occurrences of such ophiolite-type rocks in the Eastern Transylvanide Nappes, as remnants of an ophiolitic belt are mainly restricted to Rarau, Haghimas and Persani areas. They generally present under the forms of olistholithes and blocks associated to the wildflysh deposits. The ophiolitic fragments are mainly made up by lherzolitic ultramafics, basalts and serpentinites, in the Persani area. Among them, harzburgites are the most common (Hoeck *et.al.* 2006).

The Triassic ophiolites from Persani Mts. are listed as part of the Olt Nappe by Sandulescu (1984), with occurrences in Tepeu Valley at Racos, and Ceapa- and Surmanului Valley at Vârghis. In the Surmanului Valley two serpentinite blocks are incorporated, among the ophiolites, in the wildflysch deposits (Cioflica *et.al.*, 1965).

One of the most important group of minerals related to ophiolitic sequences are zeolites, and they can have the role of index minerals in ocean-floor, low-grade regional, or burrial methamorphism sequences (Liou, 1971; 1979), e.g. the zeolite facies of regional metamorphism. In such systems, association of zeolites with prehnite, pumpellyite, lawsonite or albite would be as normal. The ophiolitic sequences of Apuseni Mts. are known for their well developed zeolite associations (Bedelean, 1970; Kristály *et.al.*, 2003; Kristály & Szakáll, 2006). Natrolite from Vârghis was first time indicated by Budai (1886), from the diorites of Surmanului V. He also indicated a "Calciumzeolith" associated with natrolite, which is likely to be identical with the prehnite discussed in this study.

Prehnite, as another index mineral of low-grade metamorphic systems, has its stability at higher stage than zeolites, regarding the p-T system of metamorphic processes. A series of transformation processes for the p-T conditions of regional metamorphism for zeolites – prehnite were experimentaly set, like transformation of wairakite to prehnite and kaolinite. According to Liou (1979), an ideal range of assemblages for upper values (T between 200-400 °C, $P_{fluid} \sim 1000$ bars) of "ocean-floor" metamorphism would be as follows: thomsonite + laumontite + albite to wairakite + analcime + thomsonite to prehnite + albite. A low-grade

metamorphic prehnite-pumpellyite series was identified in the South Carpathians (Szakáll *et al.*, 2002), but prehnite was indicated for the Raul Doamnei diabases from Cernat (Szakáll *et al.*, 2002), also.

The subject of the present study is the description of the mineral association from the veins of ultrabasites related to the serpentinite in Surmanului Valley. This association was not been described for this location till now.

Materials and methods

Samples were collected from an abandoned quarry, opened in a serpentinite body in the Surmanului Valley. A large number of secondary veins with colourless hexagonal platy crystals and needles, cross-cutting the veins of chrysotile asbestos are characterize these serpentinite bodies. Samples were prepared from the veins under stereomicroscope to identify the phases.

Phase identification was performed by a Bruker D8-Advance X-ray Powder Diffractometer at the Department of Mineralogy and Petrology, University of Miskolc. The evaluation of results was done by search/match operation and pseudo-Voight algorithm Full Profile Matching (FPM) operation of the EVA-Diffracplus evaluation software of Bruker.

Results

The XRPD compositions of the vein-hosting rocks are dominated by cummingtonite, albite, clinocllore and prehnite.

A series of veins, filled with aragonite-needles (Fig.1) and another series (platy crystals) with prehnite was distinguished after the first set of analyses.

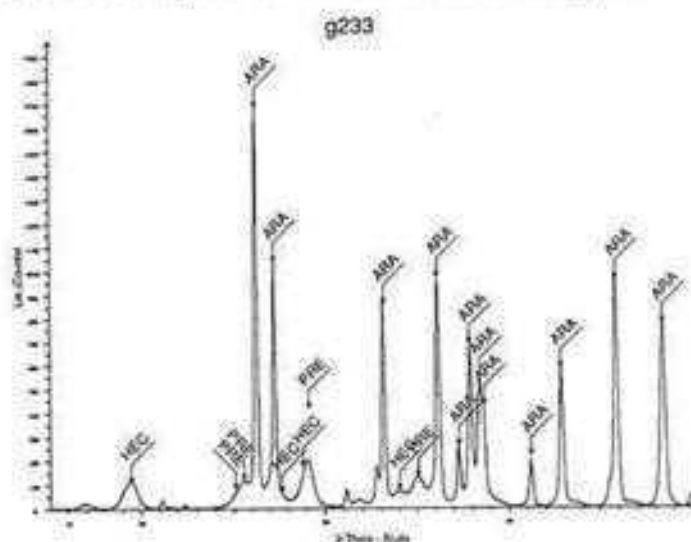


Fig. 1. FPM fitted XRPD pattern of sample G233 (HEC-hectorite, PRE-prehnite, ARA-aragonite) (Cu, $\lambda=1.5406$, 40 kV, 40 mA).

Further analysis by X-ray Powder Diffraction (XRPD) and Energy Dispersive Spectrometry (EDS) have revealed the presence of two zeolites: natrolite and analcime (Fig.2), associated to the prehnite from the veins. Chlorite-serpentine (Fig.3) and hectorite-16A (Fig.1) was also, identified in the XRPD patterns of prehnite samples.

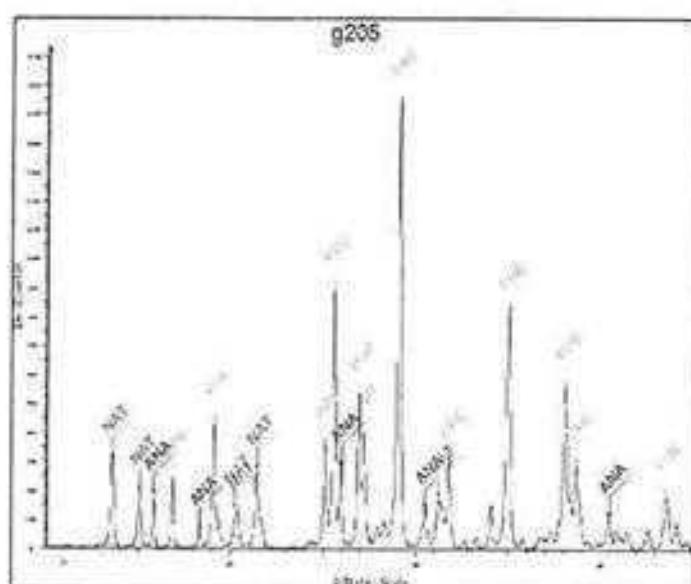


Fig. 2. FPM fitted XRPD pattern of sample G 205 (NAT-natrolite, ANA-analcime, PRE-prehnite) (Cu, $\lambda=1.5406$, 40 kV, 40 mA).

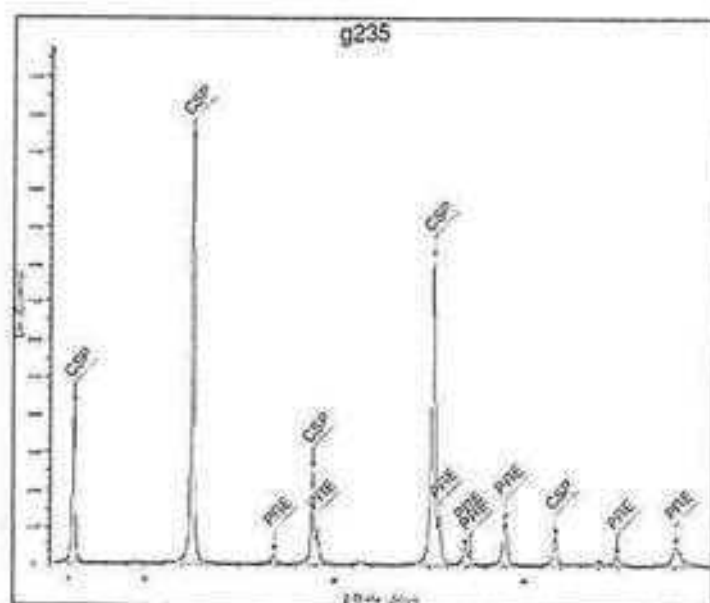


Fig. 3. FPM fitted XRPD pattern of sample G235 (CSP-chlorite-serpentine, PRE-prehnite) (Cu, $\lambda=1.5406$, 40 kV, 40 mA).

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**CARBONATECYANOTRICHITE WITH AN ALLOPHANE – HALLOYSITE –
GIBBSITE ASSEMBLAGE FROM THE BĂLAN COPPER ORE DEPOSIT
(BĂLAN HILL), ROMANIA**

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Introduction

The Bălan copper ore deposit is situated in the northern part of the Ciuc basin, developed in the epimetamorphic (retrograde) schists of the Tulghes lithogroup. In the central part of the NW – SE elongated deposit, in the Bălan Hill a polymetallic type sector was developed, being extracted in the Franz Ferdinand quarry. Samples of the oxidation zone of this body were preserved mostly in the 19th century collections, but fortunately in a corner of the quarry we were able to find a small fragment of the oxidation zone mostly unexploited.

Ackner (1855) was the first, who mentioned minerals from the Bălan deposit as azurite, cuprite and malachite. Later Koch (1885) added to Ackner's data hematite, pyrite, chalcopryrite, bornite, chalcantite and chlorite. Băncilă and Gálfi (1987) characterized the oxidation zone as being composed mainly from "limonite", quartz, malachite, azurite, chrysocolla, chalcosine, covellite, and bornite.

Recently (Szakáll *et.al.* 2006) the presence of a rare Cu mineral, carbonatecyanotrichite was identified among malachite, azurite and brochantite, associated to the allophane encrustations. The aim of the present study is to clarify the relations between these minerals.

Materials and methods

Samples from the Franz Ferdinand quarry from Bălan were collected recently, from a remnant of the oxidation zone. The general appearances of samples are that of light blue encrustations in fissures and voids of a material generally made up by limonite and manganese oxides admixture and quartz. The iron oxy-hydroxydes are supposed to be formed by the weathering of iron ore minerals, while the quartz is remnant of the host rock quartz veins. The majority of the rock-forming minerals were transformed by the weathering. On the

surface of the blue allophane crusts are small groups of millimeter sized azurite prisms, malachite and spheres of tiny brochantite needles. Light blue carbonatecyanotrichite needles were found in pores of the limonitic mass, accompanied by brochantite.

For determination of the minerals by X-ray Diffraction (XRD), the different minerals were handpicked under stereo-microscope. The samples were analyzed by a Bruker D8 Advance diffractometer (Cu, $\lambda=1.5406$, 40 kV, 40 mA), equipped with Göbbel Mirror at the Department of Mineralogy and Petrology, University of Miskolc. Scanning Electron Microscopy (SEM) images and Energy Dispersive Spectrometry (EDS) measurement was performed on an AMRAY 1830i/T6 scanning electron microscope, at the Department of Metallurgy, University of Miskolc.

Results

Due to minutious observations by optical microscope and analyses of small amounts of pure samples, we were able to distinguish between several important components of the assemblage. The blue colored crust, mentioned to be allophane, proved to be a mixture of halloysite, gibbsite and allophane (Fig. 1, note the background elevation caused by allophane in the XRPD pattern of sample G 214a).

The halloysite appear as lamellar aggregates, overgrown by allophane, while gibbsite forms thin crusts in the fissures or on the surface of allophane covered spheres (Fig.2). Results of the XRD analysis for halloysite and gibbsite are given in Table 1.

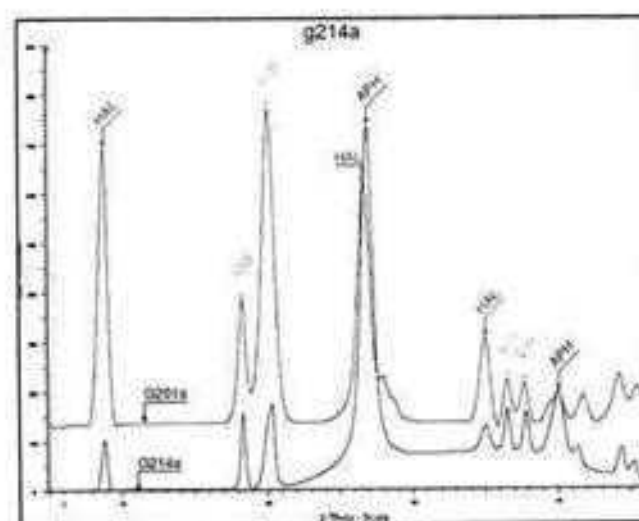


Fig.1. Full Pattern Matching (FPM) fitted XRPD pattern of „allophane” samples (HAL-halloysite, GIB-gibbsite, APH-allophane)

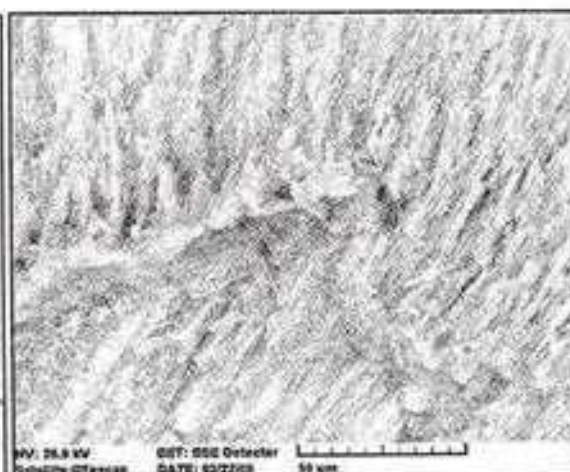


Fig. 2. SEM image of an allophane sample. The glass like crusts have a fibrous, lamellar structure, due to mixing of malloysite, allophane and gibbsite.

Gibbsite	#001-0263 (D)		g214b		g201a	
Lines	d(Å)	I%	d(Å)	I%	d(Å)	I%
(002)	4.850	100	4.835	91	4.8422	100
(110)	4.370	84	4.377	100		
(311)	2.460	59	2.455	54	2.45509	34
(-311)	2.380	59	2.375	52	2.38115	31
(313)	2.050	41	2.041	37	2.04619	39
(314)	1.800	41	1.798	36	1.80264	24
(024)	1.750	41	1.747	36	1.74983	24
(-124)	1.690	41	1.693	39		
(220)	2.170	25	2.180	21	2.16181	21

Halloysite	#029-1489 (*)		g214b		g201a	
Lines	d(Å)	I%	d(Å)	I%	d(Å)	I%
(001)	10.000	100	10.075	100	10.067	100
(100)	4.360	70			4.412	114
(003)	3.350	40	3.328	59	3.331	87
(110)	2.540	35	2.557	43	2.560	31
R/R0			5.08		4.79	
RWP %			22.6		16.3	

Table.1. XRPD results and FPM fitting report for gibbsite and halloysite.

Some overlapping (o.l.) of the reflections by accompanying phases occur. (R_{wp} weighted reliability of FPM fitting. $R=R_{wp}$ - $R0$ discrepancy)

In a few samples clinochlore was identified on the XRD pattern (Fig. 3), but we could not prove the same phase by chemical analyses. The presence of malachite and azurite was confirmed by XRD. Brochantite (Fig. 3) was identified near the clinochlore like phase. The light blue needles from the voids of the limonitic mass are carbonate-cyanotrichite (structure not refined, $Cu_4Al_2(CO_3,SO_4)(OH)_{12} \cdot 2H_2O$.) according to EDS analysis (Fig. 4) and XRD investigations (Fig. 5).

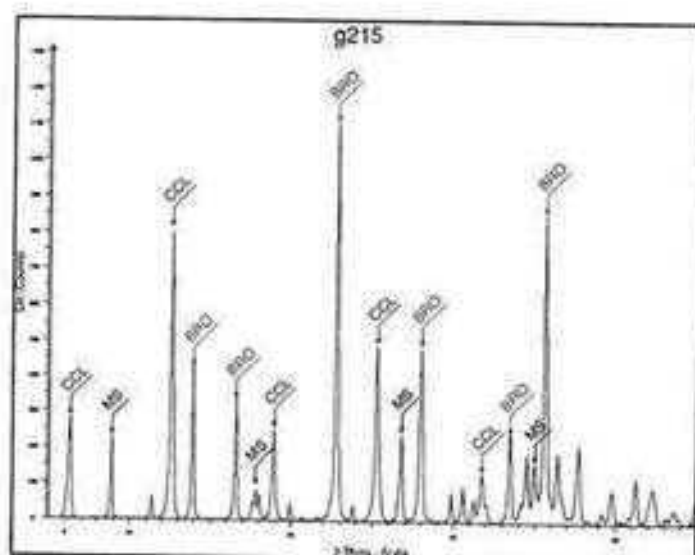


Fig.3. FPM fitted XRPD pattern of sample G215 (CCL-clinochlore, MS-muscovite, BRO-brochantite).

In spite of the careful preparation of the samples, chalcoalumite ($Cu^{+2}Al_4SO_4(OH)_{12} \cdot 3H_2O$, monoclinic) is present on the XRD pattern of sample (Fig. 5), probably indicating the presence of a transformation process.

Carbonate cyanotrichite was found in similar association at Rudabánya (N-Hungary), as its first occurrences in the Carpathians, where it occurs in cavities of the

limonitic blocks, accompanied by malachite and brochantite (Szakáll, 2001).

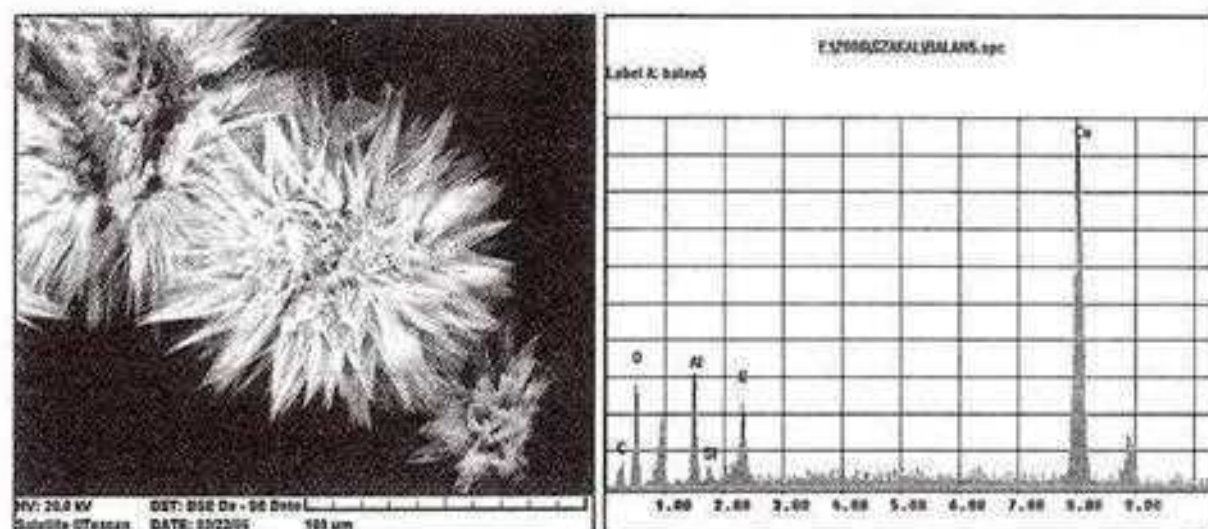


Fig. 4. SEM image of carbonate-cyanotrichite needles (left) and the EDS spectrum of the specimen.

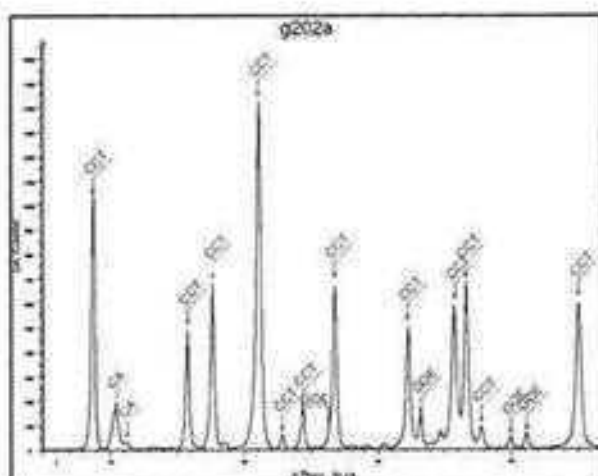


Fig.5. FPM fitted XRPD pattern of sample G202a (CCT-carbonate-cyanotrichite, CA-chalcoalumite, GOE-goethite).

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NON-CONVENTIONAL USES AND NEW PRODUCTS FROM QUATERNARY BASALTS

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INTRODUCTION

The Quaternary basaltic rocks are among the recent magmatic products located in the eastern part of the Alpine-Carpathian-Himalayan mountain chain on the Romanian territory. The emergence region of the most recent basalt products is situated in two areas: one in the center of the country, in the Persani Mountains, situated about 70 km away from the city of Brasov; the second area is the Banat region, situated in the western part of the country (Marica, 1991) (Figure 1).

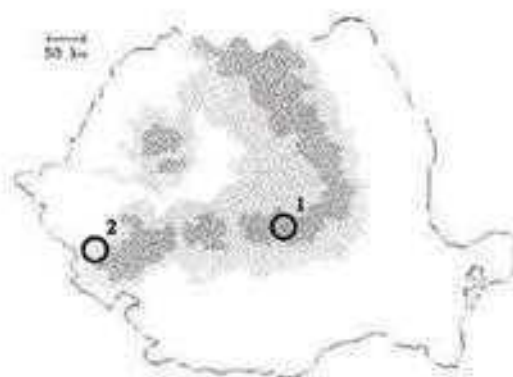


Figure 1. The emplacement of the two investigated areas:
[1] Persani Mountains, [2] Banat region



Figure 2. Volcanic bomb and scoria fragment in the Banat deposits

GEOLOGICAL INFORMATION

The basaltic rocks are the result of the intraplate magmatic activity in the Transylvanian - Pannonian block from Romania and Hungary, following alpine consolidations. Volcanic break out centers generated along a NE-SW alignment that marks fractures of the lithosphere belonging to the most recent geological periods, continuing south of the Danube. Racos zone from Persani Mountains is the best known and spectacular zone with typical features and varieties of vacuolar basaltic rocks.

The lavas emitted during such an activity had basaltic affinity, but it were, mostly, quite viscous and accompanied by large quantities of gases, which determine the explosive and permanent character of the activity. The activity consisted in rhythmic and continuous

explosions, of lava rich in gases and vapor. This resulted in fragmentation of the lava and the formation of bombs and scorias. (Fig. 2).

The petrographic and mineralogic characteristics, rendered from geological research and microscopic study are those of sand, common for all basalts types. They structure a megascopic appearance of black or brownish or reddish color for scorias, with massive, vacuolar or scoria textures. The chemistry of all studied basaltic lavas confirmed their alkaline character, similar to that of many types of basalt in the world (Marica, 1991; Marica et al., 2003).

RESULTS

To obtain new and non-conventional products – namely the glazed basalt tiles – the basalt cut slab were subjected to different tests in order to define the properties of these rocks and to compare them with similar -known products such as ceramic floor tiles. The tests proved that basalt tiles have got better properties than floor tile bodies. The experiments performed included three processes, coating with frit glazing and classic kiln baking, cold coating and coating with glazes.

The basalt proved to present very good cutting parameters and linear thermal expansion in a temperature range of 5.67 and $8.85 \times 10^6 \text{C}^{-1}$ for basalts. The classic ceramic coating process used glazes with grinding fineness of $0.16 / 0.20 \text{ mm}$, the liter weight of 1620 g/l and Galenkamp fluidity of $5-6^\circ\text{C}$. The resulting surfaces are glossy, uniformly covered from a decorative aspect and by a variety of colors, resistant to various external and internal impacts.

To obtain the final products - namely the glazed basalt tiles - the basalts samples have been subjected to physico- mechanical and physico- ceramic tests (Fig. 3, 4) in order to get acquainted the properties of these rocks and to compare them with similar, already known products as are, the ceramic floor tiles.

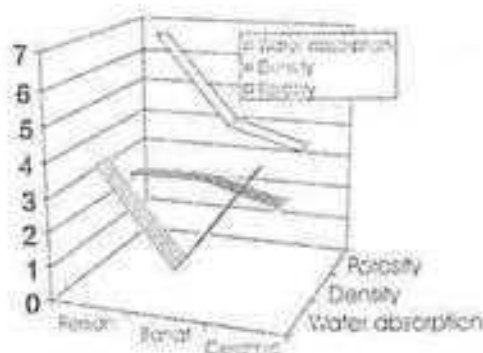


Figure 3. Comparative physical characteristics of glazed basalt tiles and ceramic tiles



Figure 4. Comparative mechanical characteristics of glazed basalt tiles and ceramic tiles

The obtained results, on the two variants of rocks using three technological methods and film covering were very satisfactory, even exceptional so, more especially for the tiles with basalt vacuole support, supporting the exposal for a domestic production of such tiles.

The covering with easily fusible glazes took into account the physico-chemical and mineralogical characteristics. Two main direction for making glazing were firing at temperature between 920 and 9800C and the second method was the use of low temperature glazes (glossy opaque or mat) whose melting temperature is between 950 and 10000C.

The third method applied included functional organic coverings. These are combined coverings of the vacuolar basalt plates and included stiffening materials in the hollows the basalt tiles that have been cut. The following stiffening materials may be used: inorganic or organic granules, fibre wastes, broken glasses, slags, industrial sub- products (steriles, basalt sand, red mud) (Marica et al., 1999).

The cold coating process used organic and epoxy resins, various wastes and ceramic pigments The resulting surfaces display a rustic aspect, suitable interior decorations.

The techniques of glazes applications included: stencil process (Fig.6); manual brushing process; pulverizing process; painting.



Figure 5. Drying process of glazed tiles samples



Figure 6. The cover of basaltic tiles with glazes by stencil process

The special characteristics of basalt rocks may be an ideal material base for obtaining certain slabs/tiles with various dimensions and formats that gain a special appearance after having been coated with glazes (Marica et al., 1999) (Fig.7).



Figure 7. Basaltic slabs covered by inorganic glazes, with various colors and decorative aspects

Conclusions

The special characteristics of Quaternary basaltic rocks from Romania can be an ideal material base for obtaining decorative and multifunctional tiles with various dimensions and formats that gain a special appearance after having been coated with glazes.

Such tiles may be used in various fields such as: interior and exterior cladding of walls and floors with intense circulation, bathrooms, entrance halls, stairs or other interior facing walls or other surfaces in special environments that are exposed to frost, heat or those exposed to corrosion and acids.

The non-conventional coating by oxy-gas flame thermal spraying process used basalt frits with a grinding fineness between 100 and 70 μm , resulting in rough, dark colored surfaces, suitable for floors with high compressive strengths.

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CORRELATIONS BETWEEN COLUMBO-TANTALITES BEARING PEGMATITES FROM NORTH SERRA DOURADA MASSIF (GOIÁS) AND FROM MIDDLE EAST REGION OF THE PEGMATITIC EASTERN PROVINCE (MINAS GERAIS)

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Introduction

The columbo-tantalites from this study were collected in pegmatites bodies from the middle east region of the Eastern Pegmatitic Province (Minas Gerais, Brazil) and from the north region of the Serra Dourada Massif (Goiás). Sampled columbo-tantalites sizes ranges 1 to 10 cm. Microprobe analyses were performed at the Ecole des Mines de Paris, France. The purpose of this investigation is the comparison between columbo-tantalites from these two different sources.

Geologic Settings

1 - Middle east of the Eastern Pegmatitic Province (EPP): these pegmatites are localized in the eastern bord of the São Francisco Craton (Mariano et al. 1991). The pegmatites bodies show variable sizes between 50 to 100 m long and 0.5 to 2m thick and are hosted in either the Gneiss de Guanhães (Silvano in Dorés de Guanhães-MG, Barra Cachoeira, Morro Escuro, Ponte da Raiz in Santa Maria de Itabira-MG), or orthogneiss (Generosa). All of those pegmatites are exploited except for Barra Cachoeira and Ponte da Raiz for beryl (the best aquamarines from Brazil).

The studied pegmatites are zoned, and have tabular or lenticular shapes. Garnet, fluorite and the topaz occur in all bodies. The euxenite (22% TiO₂) is identified in Generosa pegmatite and samarskite is found at Ponte da Raiz pegmatite.

2 - Pegmatites from north region of the de Serra Dourada Massif SDM : The north area of the SDM (Lower Paleoproterozoic; Macambira, 1983) and the country rocks are cut by an post-tectonic pegmatite granite and by general pegmatites bodies (Neoproterozoic, Marini *et al.*, 1984). The pegmatite granite (Bilal, 1991) outcrops in an area about 18 km². Irregularly disposed, laying both conformally, unconformally with orientated foliation on micaschistes or granites of SDM. Their enclaves are blocs from micaschistes and quartzites. The pegmatite mineralogy is fine medium grained milky quartz, muscovite cloths sometimes

radiated, biotite, K-feldspar, albite and garnet. The veins of quartz, albite and micas are associated to these facies. Their variable sizes ranges from 20 cm to 10 m. They are mineralized with beryl, columbo-tantalite and tourmaline. They have the same minerals as in pegmatitic granite. The yellow-green beryl (2 to 10 cm) is associated to muscovite and feldspars. The black greenish tourmaline is an inclusion in the milky quartz. The columbo-tantalites are frequent and their sizes are up to 2 cm. The garnet (0.5 to 1 cm) is sometimes embedded in feldspars. The MnO contents of garnets depict a subtle decrease with a slight falling from pegmatitic granite (11.81 to 12.15 %) to pegmatites (11 to 8 %) but the Fe contents remains uniform. The Fe/Mn ratio of this garnets remains very high (3 to 2) showing the primitive signature of this pegmatites and, in more fractioned pegmatites, this ratio is about 0.01 or less (Cerny *et al.*, 1985). Fluorine minerals were not recorded in these pegmatites.

Chemical composition of columbo-tantalites

1 – General evolution:

Columbo-tantalites of the EPP region are associated to euxenite (22% of TiO_2) and to samarskite. Showing an increase in TiO_2 (up to 3.75%), this evolution towards manganocolumbites and manganotantalites is seen in Fig.1. In the other way, evolution of columbo-tantalites from NSDM pegmatites points towards ferrotantalites fields. The role of the garnet in fractionating Mn is negligible because it is present in both areas and couldn't give contrasting evolutions explanations for columbo-tantalites. Manganocolumbite and spessartite show the extreme Mn fractionation in pegmatites of the EPP middle east region. These dual behaviors between those regions are due to the presence of fluorine (fluorite and topaz) in EPP pegmatites and lacks in those pegmatites from north SDM. Shaw (1974) and Hildreth (1979, 1981) argue that Mn is one of those cations that enriches during differentiation and are explained by their volatiles contents (H_2O , F, etc.) affinities by silicate liquids. It is clear that Mn could be complexated by fluorine and remains in liquidus and fluids phases until a final consolidation phase (Shaw, 1974; Bailey, 1977; Cerny *et al.*, 1985).

2 - Elements distribution of different sites:

The columbo-tantalites have a structural formula AB_2O_6 (A = Fe and Mn; B = Ta, Nb, Ti, Sn and W).

The diagram Ti+Sn+W versus Ta + Nb (fig.2), stressing the role of the main elements of the B site, shows that columbo-tantalites are disposed by three straight regression lines: the first group of columbo-tantalite fits the line (1). This group shows excesses in B site by the Ti

introduction in the structure. Actually, these columbo-tantalites are Ti enriched and are associated to euxenite. The second group fits line (2) of -1 declination, representing the saturation of B site. These columbo-tantalites have normal Ti contents. The third group of columbo-tantalite, essentially in the north area or the SDM, shows a deficit in B site and is fitted by line (3). These columbo-tantalites are Ti-poor.

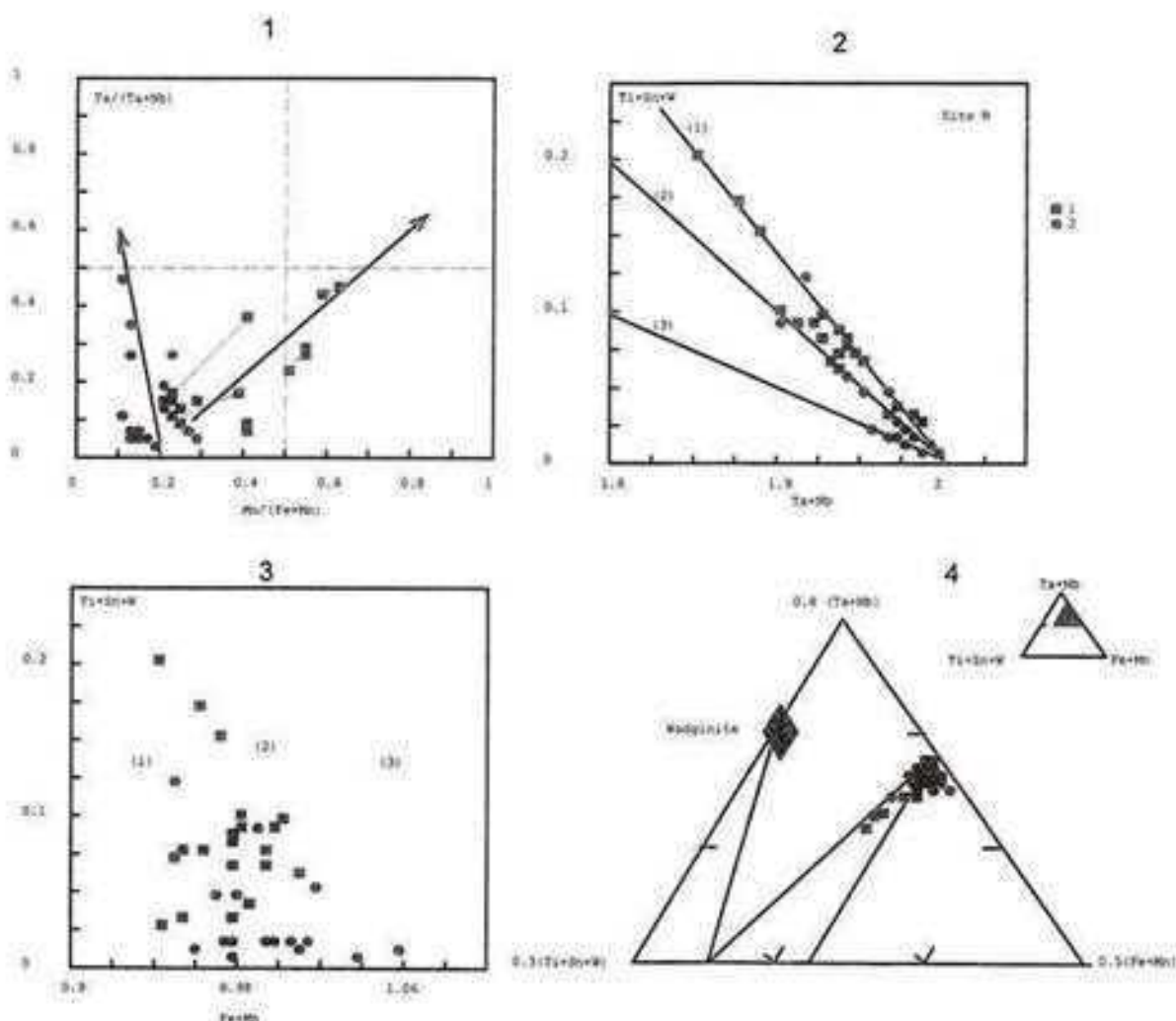


Fig.1. Compositions of Columbo-tantalites variations in diagrams Ta/(Ta+Nb) versus Mn/(Mn+Fe). 1 : columbo-tantalites from middle east EPP (Minas Gerais), the traces between points are variations observed in crystal scale; 2 : columbo-tantalites from NSDM (Goiás).

Fig.2. Variation of Ti+Sn+W in relation to Ta+Nb in B site of the columbo-tantalites structure. Same symbols as in Fig.1.

Fig.3. Relation between Ti+Sn+W of B site and Fe+Mn from A site of columbo-tantalites. Same symbols as in Fig.1.

Fig.4. Variation of studied columbo-tantalites in diagram (Ta+Nb)-(Fe+Mn)-(Ti+Sn+W). Same symbols as in Fig.1.

The diagram Ti+Sn+W versus Fe+Mn (fig.3) shows that columbo-tantalites of the second group are around the line Fe+Mn = 1. By the other way, those from first and third groups show a deficit and an excess in A site respectively.

3 - Structural implications

There is a problem in rigorous application of the structural columbo-tantalite formula AB_2O_6 in the first and third groups. There is an compensation between A and B sites for columbo-tantalites. Only the usual substitution mechanics of the columbo-tantalites in different sites could not explain the distribution of these elements. Their structure could be explained by structure disordering of the pseudoixiolite type. These columbo-tantalites are in fact settled in the pseudoixiolite field (fig.4).

Conclusions

The chemical composition of columbo-tantalites could show structure disorders without systematic use of diffractometer. The difference in the evolution of the columbo-tantalites compositions from NSDM pegmatites in relation to EPP columbo-tantalites is in the role played by the F in the Mn complexation. The extreme enriching in Mn is general rule for associations of minerals like lepidolite and microlite F- rich.

Acknowledgments

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RARE ALKALI METAL LITHIUM FROM GRANITIC PEGMATITES AS METALLOGENETIC INDICATOR FOR THE RARE ELEMENTS

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Granitic pegmatites have always aroused the researcher's interest by their interesting features, regarding structure, petrography, mineralogy, geochemistry, metallogenetic potential and genesis. Granitic pegmatites are a classic example of diversified sources: optical quartz and fluorite; feldspars; micas; ceramic amblygonite and spodumene; rare elements (Li, Rb, Cs, Be, REE, Y, Sc, Zr, Hf, Nb, Ta, Ga; Smirnov et al., 1986); radioactive elements (U, Th); other elements (Ti, Sn, B, F, P).

The classification of granitic pegmatites can be subdivided in the four classes (Table 1).

Table 1. Classification of granitic pegmatites (Černý, 1992)

Class	Families	Type	Subtype
1. Abyssal			
2. Muscovite			
3. Rare element	NYF	Rare earth	Allanite + monazite
			Gadolinite
	LCT	Beryl	Beryl + columbite
			Beryl + columbite + phosphate
	LCT	Complex	Spodumene
			Petalite
			Amblygonite
			Lepidolite
	LCT	Albite-spodumene	
	LCT	Albite	
4. Mirolitic	NYF		

Subdivision of the rare-element class pegmatites utilizes several criteria such as bulk chemistry, geochemical signature of accessory minerals, internal structure and P-T condition of crystallization (Černý, 1992):

1. *rare earth type*: is characterized by significant presence of REE, Y, Nb, Ta, Zr, Ti, Li, Be, U, Th, F. Depending on the contents of REE in the bulk composition of a pegmatite, it

is possible to distinguish an allanite + monazite subtype (LREE enriched) and a gadolinite subtype (HREE and Y);

2. *beryl type*: is marked by increased content of Be accompanied by $Nb \leq Ta$ in the beryl- columbite subtype, and also by phosphates of Ca, Mg, Fe, Mn, Cr in the beryl-columbite-phosphate subtype;

3. *complex type*: is characterized by the presence of substantial contents of Li, Rb, Cs, Be, $Ta > Nb$, Sn, Ga, P, B, F; the spodumene subtype is the most common variety. Other subtype: petalite, ambylgonite, lepidolite (HREE, Y) pegmatites;

4. *albite spodumene type*: mineralization is restricted to substantial Li, with or without subordinate Be, Nb, Ta, Sn;

5. *albite type*: albite > quartz; mineralization is sparse (Nb+Ta, Sn, Ti, Be).

This types of granitic pegmatites can be subdivided into three principal families: LCT pegmatites (Li, Rb, Cs, Be, $Ta > Nb$, Ga, Sn, P, B, F); NYF pegmatites ($Nb > Ta$, REE, Y, Zr, Ti, U, F) and pegmatites with a mixed geochemical signature.

The present geochemical data from the literature and those obtained by us reveal the possibility of using the alkali rare metal Li of granitic pegmatites in metallogenetic potential evolution. The metallogenetic potential for rare elements in granitic pegmatites can be assessed using geochemical criteria and representative diagrams for pegmatites and for minerals.

The rare alkali metal Li is a typical element of granitic pegmatites. During the first stages in geochemical evolution of pegmatitic process, Li is isomorphically scattered in the crystal lattice of minerals and in the final stages, Li becomes a principal element and forms proper minerals, among all, spodumene being the most important one. Lithium preferably concentrates in the ferromagnesian minerals and in the muscovite, as a result of its affinity for Fe, Mg and Al. Li penetrates into ferromagnesian minerals following an isomorphous substitution: $Li^+ + Al_{VI}^{3+} = 2Mg_{VI}^{2+}$. The presence of Li in the crystal structure of muscovite is the result of the following isomorphous substitution: $Li^+ + 2Si_{IV}^{4+} = Al_{VI}^{3+} + 2Al_{IV}^{3+}$. Thus, $Li/Mgx10^3$ in biotite (Table 2) and in garnet (Figure 1) and $Li:(Al_{VI} + Al_{IV})$ (Figure 2) in muscovite can be used as metallogenetic indicator for granitic pegmatites.

Table 2 $\text{Li/Mg} \times 10^3$ in biotite from Romanian pegmatites*

Location	Mg (%)	Li (ppm)	$(\text{Li/Mg}) \times 10^3$
Preluca pegmatite subprovince			
Pleşei Valley	3,72	290	7,8
Ciungi	3,98	212	5,3
Copalnic	3,72	408	10,9
Sunătorii Valley	4,57	371	8,1
Rodna pegmatite subprovince			
Rebra Valley	3,98	700	17,5
Scărișoara	3,80	710	18,6
Pascaru	4,06	685	16,8
Gilău pegmatite subprovince			
Crîșeni	4,89	440	9,0
Calului Valley	8,43	320	2,3
Crîșeni	4,90	408	8,3
Getică pegmatite subprovince			
Voislova	3,55	455	12,8
Armeniș	4,10	232	5,6
Cataracte	5,10	241	4,7
	5,18	432	8,3
Conțu pegmatitic field:			
Albite – spodumene pegmatite	4,68	1854	39,6

* Apostolescu Rodica (1973); Pomârleanu, Movileanu Aurelia (1977); Murariu (2001)

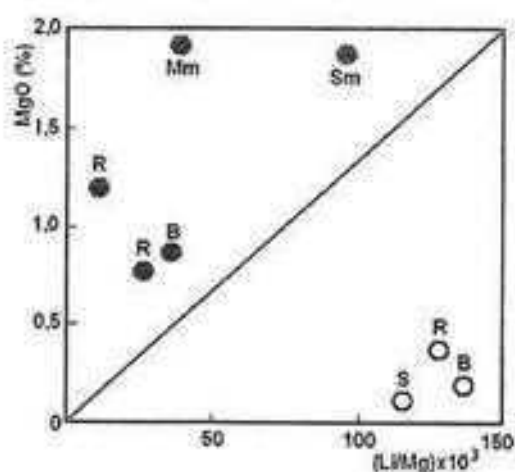


Figure 1. Projection values MgO and $(\text{Li}^+/\text{Mg}) \times 10^3$ for garnets of the unmineralized (●) and mineralized (○) pegmatites; R – garnets of the Carpathian pegmatitic province, Romania; B – Baltic shield; S – Siberia; Mm – Mamsk; Sm – Smrček (Murariu, 2001)

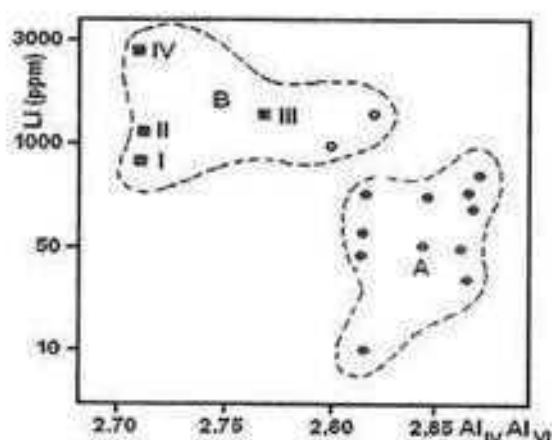


Figure 2. Diagram $\text{Li}: (\text{Al}_{\text{IV}} + \text{Al}_{\text{VI}})$
 A- unmineralized pegmatitic field
 B- mineralized pegmatitic field
 ■-muscovites of the pegmatites with rare metals (Siberia)
 ○-muscovites of the albite- spodumene pegmatites (Conțu)
 ● - muscovite of the unmineralized pegmatites (Carpathian province) (Murariu, 2001)

Similar results have been obtained using the values C_{Li2O} from muscovite and crystallization temperature of muscovite (Eugster and Yoder diagram) (Figure 3). In Figure 3, the albite-spodumene pegmatites are plotted in the field of rare element (A) and barren pegmatites (muscovite, ceramic) in the field B.

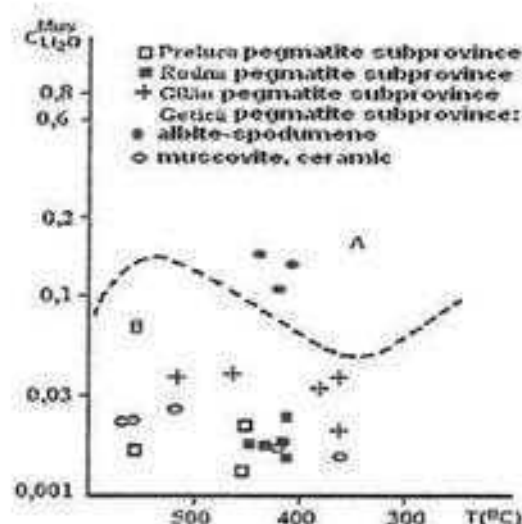


Figure 3. The metallogenetic potential of Romanian pegmatites in diagrame Mus C_{Li2O} : $T^{\circ}C$ (Murariu, 2001)

The metallogenetic potential of the granitic pegmatites can be evaluated using Trueman and Černý diagram (Figure 4).

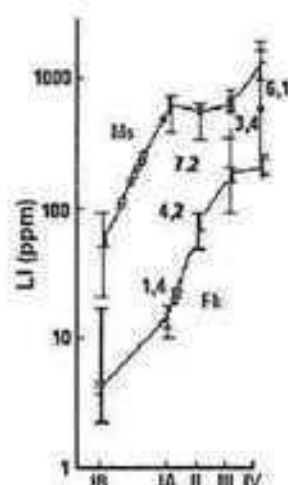


Figure 4. Li in the muscovites and potassic feldspars from Romanian pegmatites as metallogenetic indicator. IB – barren pegmatites (○). IA, II, III, IV – rare element pegmatites (●).

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Introduction

The Roșia Poieni porphyry copper deposit is a unitary structure comprising a single disseminated copper mineralized body, located in a volcanic structure formed during two distinct stages (Figure 1).

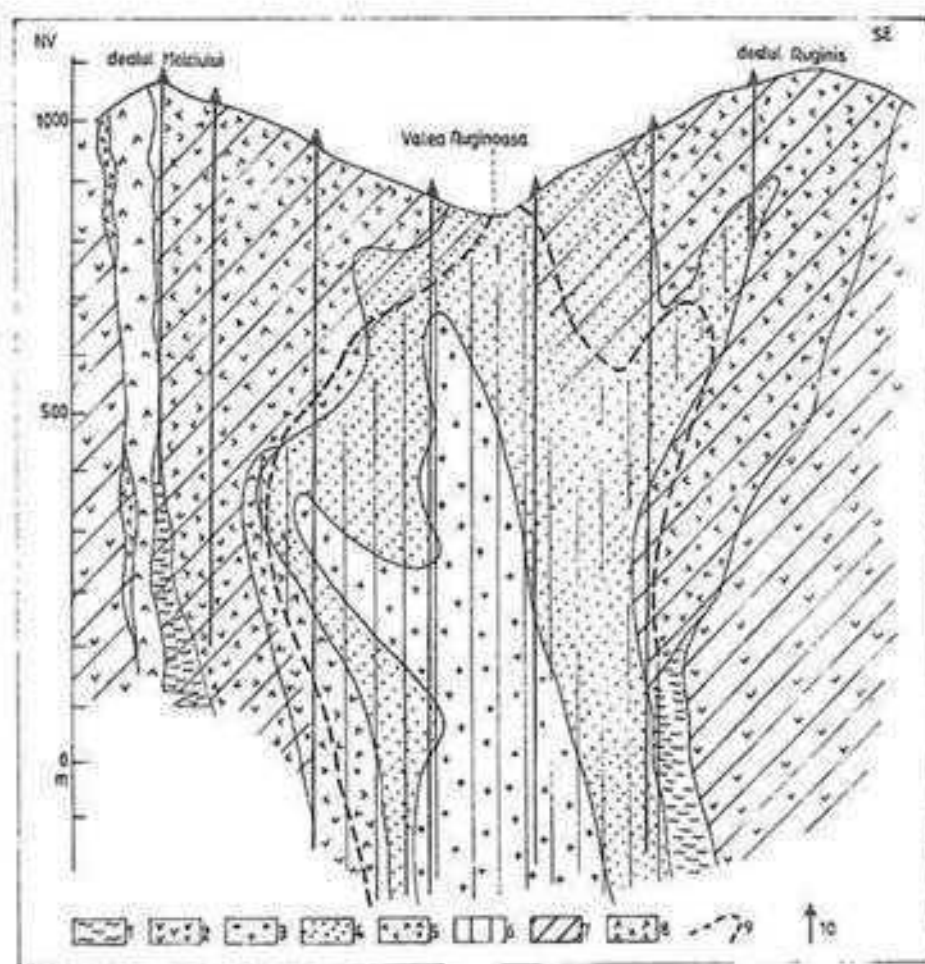


Figure 1. Geological section through the porphyry copper deposit at Roșia Poieni (after Boștinescu, 1984) 1. Cretaceous sedimentary deposits; 2. Poieni andesites; 3. Fundoia andesites (axial zone); 4. Fundoia andesites (peripheral zone); 5. Breccia; 6. Potassic hydrothermal alteration; 7. Argillic hydrothermal alteration; 8. Dealul Melciului andesites; 9. Limit of copper impregnations; 10. Drill holes.

A first stage consisted of lavas and pyroclasts which emerged from a crater of over 1 km in diameter, with adjacent smaller volcanic bodies. The subsequent volcanic eruption consisted of a porphyry microdiorite and was emplaced in the central-western part of the older

volcanic structures. Within this body, a copper stockwork structure has formed, spanning over 1200 m in height (a dense network of veinlets with disseminations of copper sulphides, iron sulphides and oxides). The mineralization is typical for what is commonly known as the porphyry copper type. Mineralized area is accompanied by a hydrothermal alteration halo with a zoned structure. The lower-central zone is occupied by potassic alteration (orthoclase and biotite) in close association with metallic minerals (magnetite, pyrite, enargite, hematite, chalcopyrite, bornite, digenite, molybdenite, tetrahedrite, sphalerite and galena). Towards the upper-external areas, sericite, argillic and propylitic areas develop, together with disseminated pyrite.

Enargite is one of the significant components of the late veining at Roşia Poieni. The analysed samples originate in the lower north east part of the Roşia Poieni open pit (Figure 2) where it occurs as vugs trapped in banded veins with dominant pyrite and violaceous quartz (Figure 3).



Figure 2. Panorama image of Roşia Poieni open pit. Arrow points to the approximate area wherefrom enargite samples have been collected.

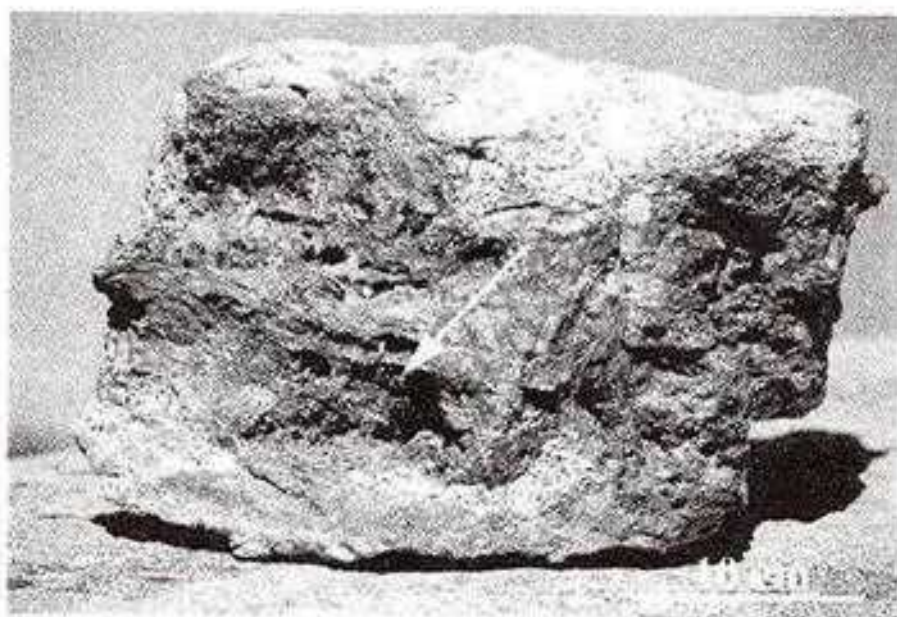


Figure 3. Hydrothermal vein fragment containing vugs with enargite (arrow), pyrite and quartz.

Under the microscope, enargite borders zoned pyrite grains or fills the interstices between pyrite grains. Enargite is partially marginally replaced by supergene covellite. In places, covellite cements clastic enargite fragments.

Chemical composition and crystal structure

Chemical analyses of enargite from Roşia Poieni were performed at the Department of Material Sciences, Division of Mineralogy, University of Salzburg, using a JEOL JXA-8600 electron microprobe, controlled by Probe for Windows system, operated at 25 kV, 30 nA, and 20 s counting time for peaks and 7 s for background. The following natural (n) and synthetic (s) standards and X-ray lines were used: n-CuFeS₂ (CuK α), s-Bi₂S₃ (BiL α), n-ZnS (SK α), n-Sb₂S₃ (SbL α), and n-NiAs (AsK α). Raw data were corrected with the online ZAF procedure.

Enargite has Cu, As and S as the main constituents; Sb and Bi are present in minor amounts, whereas Fe, Ni and Co have been also tested, but yielded no detectable concentrations. A number of 5 to 10 points were measured in three independent enargite grains. The three measured grains proved to be homogeneous but with small variations of the As to Sb ratio. The mean chemical composition is given in Table 1.

On the basis of Me = 4 atoms, the average empirical formula for the three analysed grains, may be written as Cu_{2.985}(As_{0.994}, Sb_{0.019}, Bi_{0.001})S_{4.001}, which approximates well the theoretical formula Cu₃(As,Sb)S₄, and points to a rather pure enargite (low Sb) enargite.

Table 1. Average chemical analyses of three enargite grains from Roşia Poieni (in wt %).

	Gr-1	Gr-2	Gr-3	Average	St. dev.
Cu	47.87	48.36	47.95	48.06	0.26
S	32.62	32.71	32.41	32.58	0.16
As	19.09	19.03	18.50	18.87	0.33
Sb	0.45	0.25	1.08	0.59	0.43
Bi	0.04	0.13	0.04	0.07	0.05
Total	100.08	100.48	99.99	100.18	0.26

Intensity data from an irregularly shaped crystal fragment, of approximately 0.166 - 0.120 - 0.090 mm in size, was measured on a Bruker AXS three-circle diffractometer equipped with CCD 1000K area detector and a flat graphite monochromator using MoK α radiation from a fine-focus sealed X-ray tube. The sample - detector distance was fixed at 6 cm. In all, 3165 ω -scan static exposures, 0.3° apart were made, with each frame measurement of 35 s. The SMART system of programs was used for unit-cell determination (a 7.409(1), b 6.434(1), c 6.153(1) Å, $\alpha = \beta = \gamma = 90^\circ$) and data collection, SAINT+ for the calculation of integrated intensities. The non-centro-symmetric space group $Pmn2_1$, proposed by XPREP program was chosen, which was consistent with the orthorhombic symmetry of the lattice and intensity statistics. Empirical absorption correction based on pseudo- Ψ scans, yielded a merging R_{INT} factor of 0.0584 compared to 0.1176 before absorption correction.

The structure was solved by direct methods, using SHELXS program which revealed all the atom positions. The last cycle of refinement was done by imposing anisotropic displacement for all atoms, yielding an $R_1 = 4.09\%$ for 750 $F_o > 4\sigma(F_o)$ and 4.13 % for all 763 unique reflections.

The fractional coordinates and displacement parameters of the atoms in the crystal structure of enargite are given in Table 2.

Table 2. Fractional coordinates and displacement parameters for enargite from Roşia Poieni.

ATOM	<i>x</i>	<i>y</i>	<i>z</i>
As	0.0000	0.6758(2)	0.7534(3)
Cu1	0.2518(1)	0.8300(1)	0.2433(2)
Cu2	0.0000	0.3433(3)	0.2530(5)
S1	0.0000	0.6700(4)	0.1158(5)
S2	0.2431(4)	0.8249(4)	0.6134(6)
S3	0.0000	0.3528(4)	0.6279(5)

ATOM	<i>U</i> _{eq}	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₂₃	<i>U</i> ₁₃
As	0.0151(5)	0.0156(6)	0.0161(6)	0.0137(8)	0.0000	0.0028(6)	0.0000
Cu1	0.0182(5)	0.0190(6)	0.0177(6)	0.0178(9)	0.0014(3)	0.0008(4)	0.0006(6)
Cu2	0.0318(6)	0.0331(9)	0.0361(9)	0.026(1)	0.0000	0.001(1)	0.0000
S1	0.0080(6)	0.009(1)	0.011(1)	0.004(1)	0.0000	0.003(1)	0.0000
S2	0.0299(8)	0.029(1)	0.035(1)	0.027(2)	0.0071(8)	0.007(1)	-0.007(1)
S3	0.0040(5)	0.007(1)	0.001(1)	0.005(1)	0.0000	-0.007(1)	0.0000

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PROTEROZOIC CACHOEIRA DA PRATA GRANITE MASSIF (MINAS GERAIS, BRAZIL)

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The late proterozoic Cachoeira da Prata Granitic Massif (CPGM) is located in the South zone of the São Francisco Craton, Minas-Gerais State in Southeastern Brazil. It has been emplaced (fig. 1) within granites, orthogneiss and migmatites, aged of about 2.8Gy, and volcanic and meta-sedimentary rocks of the Rio das Velhas Greenstone Belt aged 2.77Gy (U-Pb on zircons, Noce 1995).

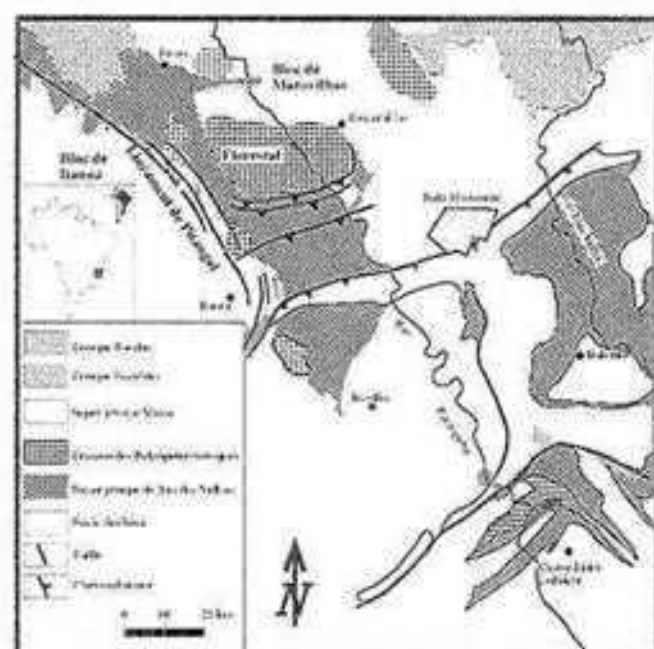


Figure 1: Geological sketch map of the western part of Belo Horizonte.

related to a monogenic regional deformation.

The CPGM presents two granitoid facies that may be recognized following their textural grain size (from fine to coarse), their structure (from isotropic to orientated in the regional trend), and their mineralogical content that presents weak variations. However those distinctive facies define a homogeneous rocks series. The granitoid rocks of the CPGM are peraluminous with an alumina saturation index (ASI) of ± 1.4 and an algaipitic index $(Na+K)/Al$ ranging between 0.60 and 0.7. The total alkali (Na_2O+K_2O) content increases from 5% up to 9% positively with the SiO_2 increase, whereas the Al_2O_3 and CaO contents decrease as a consequence of the plagioclase fractionation. Major and minor elements geochemistry of the granitic rocks of the FMG evidences a calc-alkaline series of trondhjemitic affinity.

At its eastern border the CPGM is limited by a NW-SE shear zone, named Pitangui Lineament (Romano and Noce, 1995), which is related to a collisional event between two continental blocks, a southern one (Itaúna) and a northern one (Maravilhas). The vertical to subvertical mylonitic foliation is orientated N140°. The other structural features are lineations, crenulations and folds represented by their axis, they have a same origin and they are

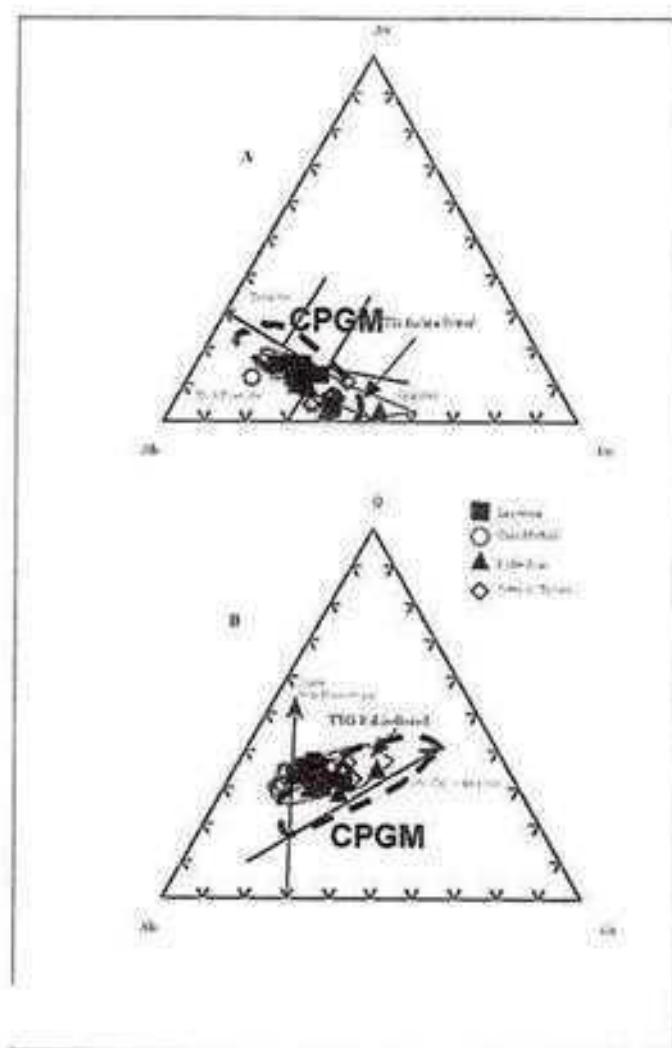


Figure 2: Normative composition of granitoids of the CPGM massif in the diagrams:

A: Anorthite-Albite-Orthose (after O'Connor, 1965, modified by Barker, 1979).

B: Quartz-Albite-Orthose (Barker and Arth, 1976)

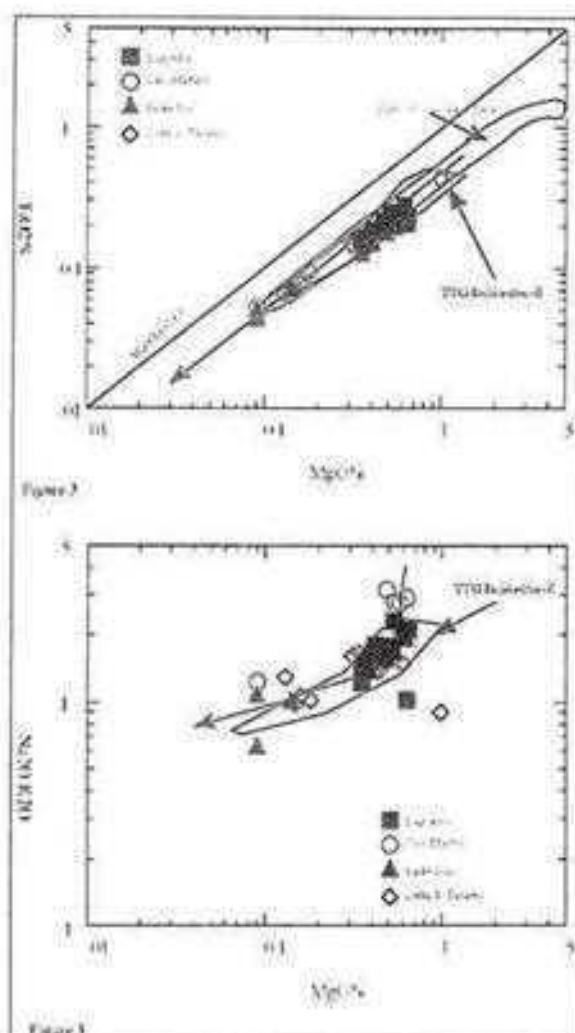


Figure 3:

A : Variations of TiO_2 vs MgO for granitoids of CPGM massif compared with the composition fields of calco-alkaline suite of Corsica (Orsini, 1980) and of TTG of Gavião block of Bahia state, Brazil (Santos Pinto, 1996).

B: Variations of (Na_2O/K_2O) vs MgO for granitoids of the CPGM massif.

Conclusion:

Taking into account low I_{Sr} ratio as well as model TDM age of 2.77 Gy granitoids of Florestal massif localized south of CPGM with the same granitoids series, an origin involving the partial melting of an early basic to ultrabasic crust mantel-accreted, as evidenced by the 2.77 Ga tholeiites and komatiites of the neighbouring Rio das Velhas Greenstone Belt, may be proposed. The CPGM would have been generated following a scenario very close to that of the western Finland TTG.

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**HIGH-TEMPERATURE AND LATE HYDROUS Ca-MINERALS IN THE
THERMALLY METAMORPHOSED LIMESTONE XENOLITHS FROM THE
BASALT OF RACOSU DE JOS, PERSANI MTS. (ROMANIA)**

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Introduction

There is a well-known basalt area in the Persani Mts., famous for upper mantle-derived xenoliths, consisting of olivine and pyroxenes (Downes et al., 1995). There are also different xenoliths of lithospheric origin, such as: conglomerates, sandstones, clays, marls, limestones, marbles, and possibly dolomites. Quartz xenoliths, contact metamorphic minerals that have been formed at the contact of xenoliths and the enclosing basaltic melt were described by Maldarescu et al. (1982). Carbonate-containing xenoliths were mentioned and examined by Marza et al. (1994). He determined high-temperature Ca-silicate assemblages with gehlenite, larnite, wollastonite, together with tridymite, quartz, feldspars and diopside in the microkarn environments. Szakáll *et. al.* (2006) mentioned levyne, ettringite and okenite for the first time from Neogene basalts of the Persani Mts.

Samples and methods

The different xenolith types were collected recently from the basalt quarries near Racosu de Jos. The presence of euhedral crystals of few minerals in the cavities is a general characteristic of all samples. The host rock has a polycrystalline, polymineralic matrix. Samples were prepared under stereomicroscope to be able to perform pure samples for the measurements. X-ray powder diffraction (XRPD) phase identification was carried out at the Department of Mineralogy and Petrology, University of Miskolc, completed with Scanning Electron Microscopy (SEM) observations and Energy Dispersive Spectrometry (EDS) at the Department of Metallurgy, University of Miskolc. XRPD patterns of samples were resolved by search/match operation and full profile matching (FPM) by pseudo-Voigt fitting algorithm with the EVA-Diffracplus evaluation software of Bruker. Detailed chemical

analyses (EPMA) were performed at the Department of Earthsciences, University of Modena Reggio Emilia.

Results

The identified minerals of the thermally metamorphosed carbonaceous (mainly Ca carbonates) xenoliths, are similar to a skarnification process. Two different mineral groups were classified on their relative temperature of crystallization (Table 1), a High- and a Low-temperature one. The matrix of the xenoliths is build up by high temperature Ca-silicate

Table 1. Genetic classification of identified Ca containing phases

Type of matrix	High temperature Ca mineral associations	Low temperature hydrated Ca mineral associations
I	wollastonite	thaumasite, erionite
II	larnite, andradite and brownmillerite	afwillite, thaumasite, tobermorite
III	gehlenite, diopside, andradite	ettringite, chabazite, levyne, okenite, plombierite

associations. On the basis of mineralogical composition, three types of associations were identified:

Type I. The xenolithe has a wollastonite matrix, with euhedral, mm-sized hexagonal prismatic thaumasite crystals (Table 2., AR_2b).

Sample	#046-1360		AR_2b		AR-B_1a	
Lines	d(Å)	I(%)	d(Å)	I(%)	d(Å)	I(%)
(100)	9.590	100	9.593	100	9.593	100
(112)	3.801	23	3.798	22	3.799	23
(110)	5.530	22	5.532	21	5.527	27
(123)	2.511	16	2.510	14	o.l	
(121)	3.423	14	3.421	12	3.421	12
(302)	2.726	14	2.724	12	o.l	
(223)	2.166	13	2.165	11	2.165	13
(111)	4.892	12	4.887	11	4.890	11
R/R0			1.76		1.95	
RWP %			15.8		13.5	

Table 2. Results of XRPD analyses for thaumasite, compared to the #046-1360 PDF pattern. Some overlapping (o.l) of the reflections by accompanying phases occur. (R_{wp} weighted reliability of FPM fitting, $R=R_{wp}$, R0 discrepancy)

Type II. This type has an andradite, larnite and brownmillerite (and babingtonite) matrix (Fig.1.) According to Shmulovich (1967) the stability of larnite in the CaO-SiO₂-CO₂ system is situated over 800 °C, for the spurrite + wollastonite = larnite + CO₂ transformation reaction. Tobermorite (and possibly rapidcreechite) occur as white earthy nests and crusts in the brownish, dark grey matrix. Euhedral, colourless, 1-3 mm-sized, lath-like or tabular crystals

The low-temperature minerals may have formed by hydrothermal processes, which affected the primary high-temperature minerals of the matrix, thus they occur in the cavities and fissures of the xenoliths. Gross (1977) mentioned a temperature of 110 °C for the formation of tobermorite, afwillite etc. by autoclaving. According to this assumption, wollastonite may have altered to thaumasite (SO₄ substitution by CO₃ identified by EDS), while alteration of the larnite-andradite-brownmillerite assemblage give rise to afwillite, thaumasite/ettringite, hydrocalumite, tobermorite (and possibly rapidcreekite). The last products are vaterite and calcite. The gehlenite-diopside-andradite assemblage could have altered to tobermorite and plombierite, ettringite/thaumasite, levyne, erionite, and chabazite. Plombierite occur in blue-white, glass-like crusts, sometimes with globular surfaces. The late-stage minerals are calcite, aragonite, vaterite and smectite.

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STRUCTURAL (ME, XRD, NGR, ESR) INVESTIGATIONS ON SOME SULPHIDES
FROM COSTESTI, VALEA LUI STAN AND JIDOSTITA GOLD ORES (SOUTHERN
CARPATHIANS, ROMANIA)

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The metamorphic rocks of the Getic Realm in the South Carpathians host several shear-zone related gold ores. These are Valea lui Stan (near Brezoi) and Costești (near Horezu) both in Căpățâna Mts., and Jidoștița (near Drobeta – Turnu Severin) in Mehedinți Mts. These occurrences are generally similar in respect to the mineralogical association (i.e. gold and sulfides in quartz lenses) and the structural settings (i.e. shear-zone related). The major minerals are arsenopyrite, pyrite, chalcopyrite and sphalerite. The differences between these three occurrences concern the geochemical parageneses (major and minor elements) and the related protore (Udubașa s., 2004).

Jidostita mineralization is located in the Mehedinți Mts. (western part of the Southern Carpathians). The ore bodies occur as folded quartz-sulfides bands or lenses, but sometimes also as veinlets. The lenses and bands are concordant in respect to the host metamorphic rocks, i.e. micaschists and gneisses assigned to the Sebes Group. The ore bodies are localized alongside a blastomylonite zone several hundreds meters wide (Iancu et al., 1980). The mineral association includes pyrite, chalcopyrite, arsenopyrite, sphalerite and galena (P. Hirtopanu, in Iancu et al., 1980), to which pyrrhotite, marcasite, rutile and rarely jamesonite (Hirtopanu et al., 1991) should be added. In the oxidation zones following minerals occur: skorodite, cerussite, smithsonite and hydrogoethite.

Costesti mineralized structure is located in the South-Eastern part of the Capatanii Mts., West of Olt River, and southwestward from the similarly featured Valea lui Stan occurrence. The ore bodies are both discordant and concordant to the fabric of the metamorphic rocks. The ore bodies are located in the paragneisses, micaschists and amphibolites of the Vaideeni Formation along NW-SE shear zones (Apostoloiu et al., 1990). Here, the biotite-blastomylonites sequences are considered the protore for the mineralization, the geochemical analyses pointing out higher Au content for this kind of rocks in respect to others. The mineral paragenesis of the Costesti occurrence is larger than the one from Valea

lui Stan. Here, pyrite and arsenopyrite prevail in the ore minerals association. Quartz, carbonates (calcite, ankerite) and chlorite are the main gangue minerals. Other ore minerals known in the paragenesis are as follows (Apostoloiu et al., 1990; Hârtoanu et al., 1991): chalcopryrite, bismuthinite, tetrahedrite-tennantite, sphalerite, jamesonite, greenockite, pyrrhotite, galena, native gold, native silver, native bismuth, wittichenite, other unidentified Bi sulphosalts (containing Bi, Pb, Ag, As, S), magnetite, marcasite, arsenolite. The Au from Costesti ores occurs mainly in arsenopyrite, sometimes associated with native Bi and Bi sulfosalts, as well as in gangue minerals (quartz). Several Au grains have been observed as inclusions in pyrrhotite (Udubasa, 2004).

Valea lui Stan mineralized structure is located in the Eastern part of the Capatanii Mts., West of Olt River. The ore bodies are both discordant and concordant in relation to the fabric of the host metamorphic rocks. The mineralization occurs mainly in the metabasic rocks of the Sibisel Group, in connection with N-S brittle-ductile shear zones related to the Getic-Supragetic Alpine nappe stacking. The protore of the mineralizations is considered to be the amphibolitic sequences of the Sibisel Group, argued by the higher Au content with respect to other (similar) rocks in the area (Udubasa & Hann, 1988). The ore paragenesis is dominated by pyrite, chalcopryrite, arsenopyrite, which are also the main host minerals for gold; quartz is the main gangue mineral. Other metallic minerals have been also described by previous authors (Petrulian, 1936; Udubasa & Hann, 1988): pyrrhotite, sphalerite, galena, tetrahedrite-tennantite, native gold, bornite, magnetite, ilmenite, hematite; as secondary minerals are cited: marcasite, goethite, covellite, chalcocite, malachite, azurite, anglesite, cerussite, scorodite. In the Valea lui Stan ores the native gold occurs as inclusions in arsenopyrite, chalcopryrite pyrite, quartz, and sometimes in goethite.

The aim of this work is to report some observable aspects, obtained by structural investigations (XRD, ME, NGR and ESR techniques) on specific samples from the above mentioned deposits. The investigated samples and the structural techniques are presented in the Table 1.

Tab. 1. The investigated samples by different structural techniques.

Label	Chemical formula	Used structural technique				Location
		EM	XRD	NGR	ESR	
assJa	FeAsS	X	X	X		Jidostita
assJa	FeAsS	X				Jidostita
sphJ	Zn(Fe)S	X	X	X		Jidostita
assCN-g01	FeAsS	X	X	X	X	Costesti - Galeria 1 Netedu
pyCN-g01	FeS ₂	X	X	X	X	Costesti - Galeria 1 Netedu
pyrCN-g03	Fe _{1-x} S				X	Costesti - Galeria 3 Netedu
pyrCN-g01	Fe _{1-x} S	X	X	X	X	Costesti - Galeria 1 Netedu
assVS-hx	FeAsS	X	X	X	X	Valea lui Stan - halda (es. VS-x)
pyVS-h	FeS ₂	X	X	X		Valea lui Stan - halda (es. VS-h)
cpyVS-h	CuFeS ₂	X	X	X	X	Valea lui Stan - halda
cpyVS-P	CuFeS ₂				X	Valea lui Stan - Petrulan

ass=arsenopyrite; sph=sphalerite; cpy=calchopyrite; py=pyrite; pyr=pyrrhotite;

The NGR spectra have obtained on sample powders at RT, using a $^{57}\text{Co}:\text{Rh}$ source (intensity of 50mCi, $a_{57\text{Fe}} = 2\%$, $f(300\text{K})=0.76$, $\Gamma_{\text{obs}}=0.22\text{mm/s}$ metallic iron foil). The spectra are showing superposed signals of ^{57}Fe in different local vicinities, characterizing by electric field gradient (EFG) and/or internal magnetic field (B). They have been analyzed by the χ^2 -criterium fit procedure. In the Figures 1, 2 and 3 are plotted the observable spectra and the preliminary fit solutions for some samples from Jidostita, Costesti and respectively Valea lui Stan deposits.

Fig. 1. Sphalerite from Jidostita (sphJ)

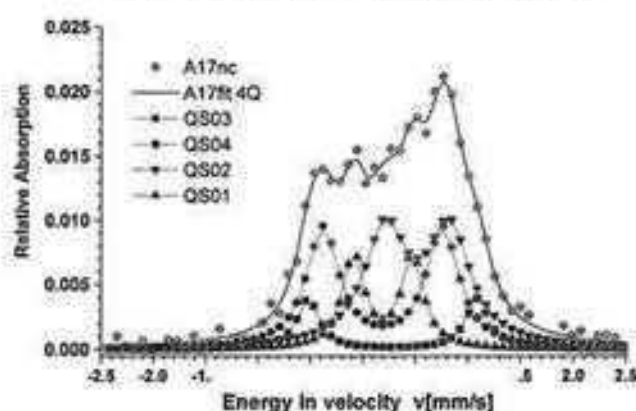


Fig. 3 Chalcopyrite spectrum, cpyVS-h

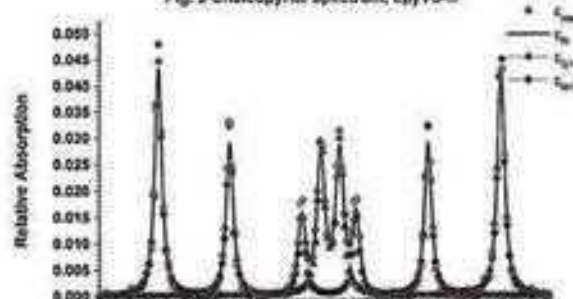
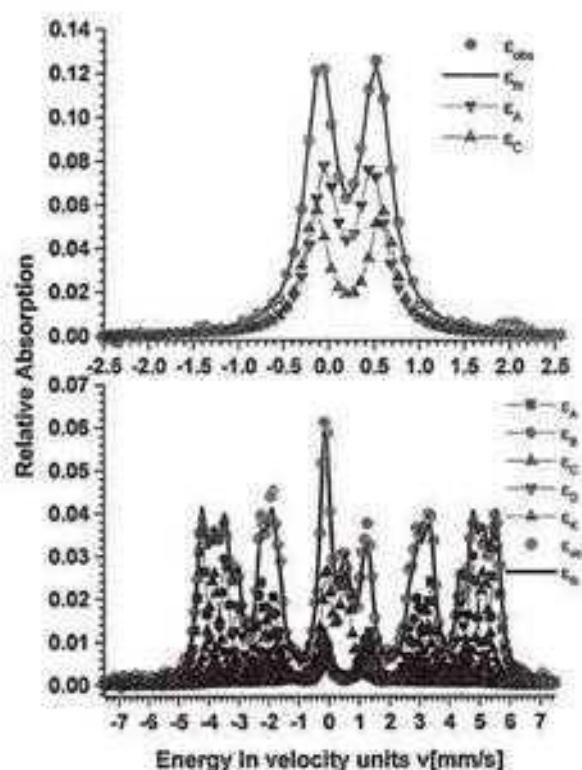


Fig. 3. Chalcopyrite spectrum, cpyVS-h

Fig. 2. NGR spectra of pyCN-g01 and pyrCNg01



The spectral parameters and some preliminary comments of investigated samples are given in the Table 2.

The XRD spectra has been obtained on the powder samples at RT, using a Seifert MZ III diffractometer, $2\theta/\text{min}=0.600$, 1000 count/s. In the figures 4-6 are plotted the XRD-spectra for some samples of Jidostita, Costesti and Valea lui Stan.

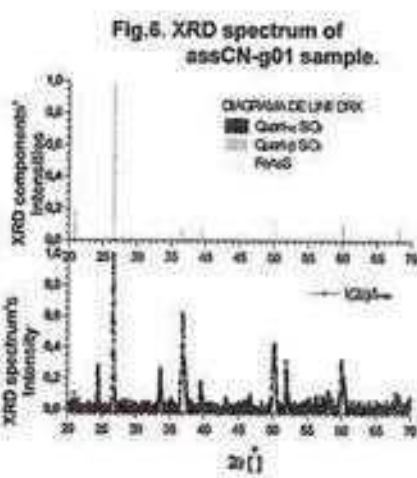
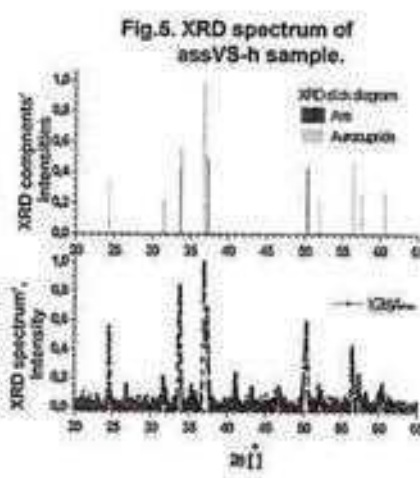
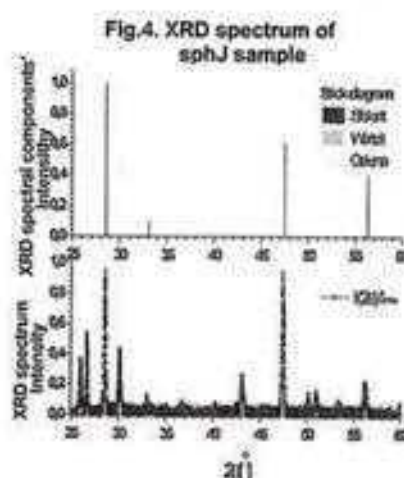
Tab. 2. Hyperfine spectral parameters of NGR investigated samples.

Sample	Fit parameters Confidence>95%		Sub- networks	δ_{iso} [mT]	Γ_{iso} [mT]	δ_{Q} or δ_{H} [mT]	B [T]	Integral area	A_{eff} [%]	Observations	
	χ^2	F									
(1) AssJa	0.9590	57.33	I II III	0.10(9) 0.16(6) 0.17(8)	0.38(9) 0.42(6) 0.24(8)	0.62(9) 1.10(6) 1.61(8)	- - -	- - -	22.80(2.5) 47.10(2.5) 18.00(2.5)	Py [1,2,4]; Fe ²⁺ octLS Ass [2]; Fe ²⁺ octLS Los [2]; Fe ²⁺ octLS	
SphJ	0.9700	594.02	Q501 Q502 Q503 Q504	0.19(1) 0.52(3) 0.19(2) 0.29(2)	0.24(5) 0.49(7) 0.38(8) 0.26(8)	0.56(2) 0.61(7) 1.14(4) 1.61(7)	- - - -	0.00565 0.01368 0.01099 0.00831	16.67(2.5) 40.77(2.5) 32.99(2.5) 9.56(2.5)	Cob [1,2,4]; Fe ²⁺ octLS Sph [8]; Fe ²⁺ octLS Ass [5]; Fe ²⁺ octLS Los [2]; Fe ²⁺ octLS	
AssCN-g01	0.9124	321.49	I III	0.14(1) 0.15(1)	0.41(4) 0.28(3)	0.98(8) 1.33(8)	- -	- -	- -	74.91(1.9) 25.09(2.1)	Ass [2]; Fe ²⁺ octLS
PyCN-g01	0.9952	7482.79	A C	0.215(4) 0.209(3)	0.33(4) 0.35(2)	0.73(6) 0.52(7)	- -	0.05731 0.07259	42.48(2.1) 57.52(2.2)	Py [1,2,4]; Fe ²⁺ octLS Mar [1]; Fe ²⁺ octLS	
PyrCN-g01	0.9879	704.06	1M 2M 3M 4M 1Q	0.597(4) 0.610(7) 0.589(5) 0.572(7) 0.214(8)	0.33(2) 0.42(4) 0.34(3) 0.31(3) 0.37(3)	0.047(4) 0.026(6) 0.063(5) 0.076(7) 0.622(8)	20.36(3) 27.79(7) 25.56(5) 22.96(6) 0.4(2)	0.07218 0.05701 0.06278 0.03640 0.02962	26.93(2.5) 25.01(2.5) 22.43(2.5) 13.58(2.5) 11.05(2.5)	FeHS; Fe ²⁺ Al+0.5A2[10] 0.5A2+0.5B1 0.5B1+0.5C1 0.5C1 Py [1,2,4]; Fe ²⁺ octLS	
AssVS-h-h	0.9639	54.78	I II III	0.14(7) 0.13(4) 0.05(1)	0.38(9) 0.44(9) 0.38(1)	0.58(7) 1.14(4) 1.71(10)	- - -	- - -	- - -	25.00(2.5) 70.52(2.1) 4.48(3.1)	Cob [2]; Fe ²⁺ octLS Ass [5]; Fe ²⁺ octLS Los [2]; Fe ²⁺ octLS
PyVS-h	0.9383	470.30	A B	0.200(5) 0.17(1.5)	0.35(1) 0.22(20)	0.631(9) 1.64(20)	- -	0.06687 0.00076	98.87(1.1) 1.13(3.1)	Py [1,2,4]; Fe ²⁺ octLS Los [2]; Fe ²⁺ octLS	
CpyVS-h	0.9938	1564.44	Q1 M1	0.207(3) 0.159(2)	0.26(1) 0.24(4)	0.626(3) 0.008(2)	- 35.5(1)	0.02467 0.07275	25.32(2.5) 74.68(2.1)	Py [1,2,9]; Fe ²⁺ octLS Cpy [2]; Fe ²⁺ octLS	

δ_{iso} - central shift

δ_Q - quadrupole splitting or shift

δ_H - quadrupole shift



The main components of the detected compounds are shown in the Table 3, for the investigated samples. The preliminary analysis of the XRD spectra evidenced the main mineral components: arsenopyrite, pyrite, marcasite, chalcopyrite, pyrrhotite, sphalerite and wurtzite, galena, auricupride, quartz for the specific deposit. One remarks the evidence of the auricupride in the *assVS*, *pyVS* and *pyCN-01* samples.

The ESR spectra have been obtained on the powder samples at RT, using a JEOL of type JES-ME-3X, which is equipped with a TE011 cylindrical cavity operating at ~9.13 – 9.15 GHz (X-band), with field modulation 100KHz.

Table 3. The XRD main lines of containing compounds in the investigated samples

Sample	h (h, k, l)	I_r	h (h, k, l)	I_r	h (h, k, l)	I_r	Comments
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
ass	33.67 [100]	0.324 0	34.78 [121]	0.3003	37.12 [112]	0.3245	Ass: $a=5.7424 \text{ \AA}$; $P1_1/\bar{P}-11213$ $b=5.6935 \text{ \AA}$ $c=5.7797 \text{ \AA}$
	26.69 [100]	0.030 2	26.69 [001]	0.1927	36.34 [112]	0.0256	Q: $a=4.9533 \text{ \AA}$; $P2_1$ $b=4.9933 \text{ \AA}$ $c=5.3055 \text{ \AA}$
	48.95 [112]	0.079 2	47.55 [000]	0.0558	46.75 [002]	0.0556	Ass: $a=3.8211 \text{ \AA}$; $Pn3m$ $b=44.8950 \text{ \AA}$ $c=3.8930 \text{ \AA}$
cpy	26.85 [111]	1.000 0	47.50 [220]	0.6150	56.36 [113]	0.0970	Sp: $a=5.492 \text{ \AA}$; $F43m$
	26.63 [100]	0.491 9	33.00 [101]	0.4850	47.02 [110]	0.3769	Wst: $a=3.6020 \text{ \AA}$; $P6_3mc$ $b=3.6520 \text{ \AA}$ $c=6.4433 \text{ \AA}$
	25.58 [111]	0.300 1	39.88 [200]	0.3209	43.85 [220]	0.2472	Gal: $a=5.9302 \text{ \AA}$; $Fm3m$
assCN_01	33.61 [100]	0.345 2	34.87 [121]	0.6977	37.23 [112]	0.3093	Ass: $a=5.7540 \text{ \AA}$; $P1_1/\bar{P}-11213$ $b=5.6645 \text{ \AA}$ $c=5.7435 \text{ \AA}$
	26.92 [100]	0.195 1	26.69 [101]	0.5900	36.32 [112]	0.1356	Q: $a=4.9500 \text{ \AA}$; $P2_1$ $b=4.9933 \text{ \AA}$ $c=5.4050 \text{ \AA}$
	20.70 [100]	0.047 3	26.52 [001]	0.4000	49.94 [112]	0.0173	Q: $a=4.9500 \text{ \AA}$; $P6_3$ $b=4.9500 \text{ \AA}$ $c=5.4050 \text{ \AA}$
pyrCN_03	29.90 [100]	0.417 9	43.66 [102]	0.9006	53.34 [110]	0.3340	Pyr: $a=3.3450 \text{ \AA}$; $P6_3/mmc$ $b=3.2450 \text{ \AA}$ $c=5.7100 \text{ \AA}$
pyrCN_08	33.82 [200]	0.565 4	37.07 [210]	0.4240	56.27 [113]	0.6830	Py: $a=5.4113 \text{ \AA}$; $Pa3$
	29.78 [110]	0.249 9	33.50 [101]	0.4535	51.60 [211]	0.3533	St: $a=4.6592 \text{ \AA}$; $Pnma$ $b=5.4682 \text{ \AA}$ $c=3.3971 \text{ \AA}$
	40.96 [112]	0.284 7	47.66 [200]	0.1900	46.68 [002]	0.1993	Ass: $a=3.8155 \text{ \AA}$; $Pn3m$ $b=44.8950 \text{ \AA}$ $c=3.8930 \text{ \AA}$
assVS-h	33.81 [200]	0.859 5	36.83 [121]	0.9658	37.59 [112]	0.8914	Ass: $a=5.7190 \text{ \AA}$; $P1_1/\bar{P}-11213$ $b=5.6785 \text{ \AA}$ $c=5.7435 \text{ \AA}$
	41.14 [112]	0.265 0	46.74 [200]	0.1655	47.75 [002]	0.1655	Ass: $a=3.8155 \text{ \AA}$; $Pn3m$ $b=44.8950 \text{ \AA}$ $c=3.8930 \text{ \AA}$
pyVS-h	33.89 [200]	0.428 8	37.13 [210]	0.3279	56.36 [113]	0.3048	Py: $a=5.4122 \text{ \AA}$; $Pa3$
	26.72 [101]	0.365 7	28.884 [100]	0.0701	58.13 [112]	0.0400	Q: $a=4.914 \text{ \AA}$; $P2_1$ $b=4.914 \text{ \AA}$ $c=5.405 \text{ \AA}$
	26.62 [111]	0.235 5	47.61 [220]	0.1440	56.49 [113]	0.0935	Sp: $a=5.3975 \text{ \AA}$; $F43m$
cpyVS-h	29.43 [112]	0.939 8	49.13 [204]	0.3768	58.82 [112]	0.3575	Cpy: $a=5.2740 \text{ \AA}$; $142L$ $b=5.2740 \text{ \AA}$ $c=10.4130 \text{ \AA}$

Ass=arsenopyrite; Cal=calcite; Pyr=pyrrhotite; Q=quartz; Wst=wustite.

Fig.7 Detail of ESR spectrum of assVS-h

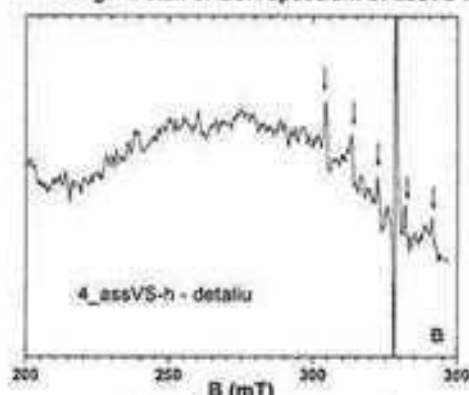
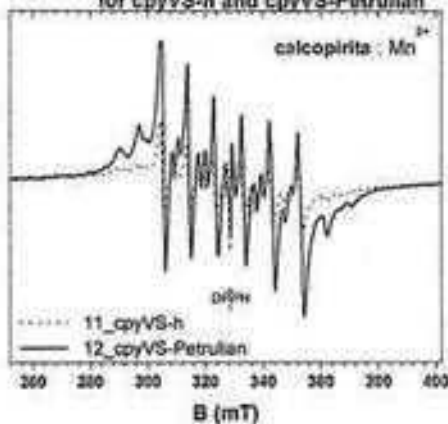


Fig. 8 Details of ESR spectra for cpyVS-h and cpyVS-Petrulian



All investigated samples are showing very large signals due to Fe^{3+} in different symmetry location. The most spectacular spectra are the spectra of assVS (Fig.7) and cpyVS (Fig. 8) in which has been detected a hyperfine interaction electron-nucleus corresponding to Mn^{2+} ions in Ca-carbonate as host matrix. The relative intensity of Mn^{2+} - ESR signal evidenced the small amounts of them.

The selected powder samples have been investigated using JEM-200 CX installation at 200KV, with TEM in bright/dark field (BFTEM/DFTEM) and SAED techniques. The main results are the evidence of:

- the nanometric precipitate with a large diversity of morphology (from isolated gold nanoparticles, some tens of nanometers in size, up to "coral-like" aggregates; for detail see Udubasa G. et al., 2006 – this volume);
- the further gold-bearing minerals i.e. uytenbogaardtite, closely associated with pyrrhotite at Costesti (see Figs. 9, 10).



Fig. 9. The evidence of Ag_3AuS in pyrCN-g01.



Fig. 10. Au precipitate particles in uytenbogaardite.

Finally one can conclude that an investigation by structural techniques as, NGR, XRD, ESR and EM on gold bearing sulfides from shear zone related ores (Southern Carpathians) have revealed further gold-bearing minerals such as uytenbogaardite, closely associated with pyrrhotite at Costesti, auricupride associated with arsenopyrite at Valea lui Stan. Moreover, during the investigations some new minerals for these ores have been identified: cobaltite in *assVS* and *assJ*, maghemite and loellingite in *sphJ*, moganite in *assC* and *assJ* and CuO in *cpyVS*.

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