**“AL. I. CUZA” UNIVERSITY**
**DOCTORAL SCHOOL OF CHEMISTRY AND EARTH AND LIFE SCIENCES**
**GEOLOGY DEPARTAMENT**
Senate decision no. 15368 from 01.10.2014

# SUMMARY OF THE PhD THESIS

## *The study of heavy minerals from the alluvial sediments of the Bistrița Aurie, Dorna and Neagra Șarului rivers*

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**IAȘI, 2014**

“ALEXANDRU IOAN CUZA” UNIVERSITY OF IAȘI

Doctoral School of Chemistry and Earth and Life Sciences

Mrs / Mr ............................................................

Please be advised that on **11/15/2014, 11:00 am, in room B6** from the Faculty of Geography and Geology, "Alexandru Ioan Cuza" University of Iasi, will take place the public presentation of the thesis entitled "***The study of heavy minerals from the alluvial sediments of the Bistrița Aurie, Dorna and Neagra Șarului rivers***", developed by PhD. Cătălina Ciortescu in order to obtain scientific title of PhD in Geology.

**Doctoral committee shall be composed:**

**President:**

**Professor Doctor Corneliu IAȚU**, Dean of the Faculty of Geography and Geology, University „Alexandru Ioan Cuza” of Iași;

**Scientific coordinator:**

**Professor Doctor Ovidiu Gabriel IANCU**, Geology Department, Faculty of Geography and Geology, University „Alexandru Ioan Cuza” of Iași;

**Reviewers:**

**Professor Doctor Călin BACIU**, University Babeș-Bolyai, Cluj Napoca, Faculty of Science and Environmental Engineering;

**Professor Doctor Gheorghe Ștefan DAMIAN**, Department of Geology, Faculty of Geography and Geology, University „Alexandru Ioan Cuza” of Iași;

**Professor Doctor Gheorghe JIGĂU**, Moldova State University, Faculty of Biology and Soil Science, Department of Soil Science, Geography, Geology, Forestry and Design.

**We invite you to attend the meeting to support the thesis.**

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## INTRODUCTION

Minerals with a high density (greater than 2.9 g / cm3), accessories constituent of silt and sediments, are known as heavy minerals. In the parent rocks they can be present both as primary minerals (amphibole, pyroxene, mica) and as accessory minerals (zircon, apatite, tourmaline), appearing in a wide variety of rocks (Mange and Maurer, 1992). Heavy minerals provide important information on understanding certain processes, such as erosion, supergene alteration, and movement of mineral particles, their genesis and correlation with a particular source. Research and study area of the PhD thesis is the Bistrița Aurie, Dorna and Neagra Șarului drainage basin. From the administrative point of view, the perimeter is mostly located in Suceava County. Geologically the stream of these three rivers crosses Crystalline-Mesozoic Zone and Călimani Complex of the Eastern Carpathians.

This paper aims to study heavy minerals from the alluvial sediments of the Bistrita Aurie, Dorna and Black Şarului rivers in order to characterize in detail the mineralogy and he chemistry. Also study aims to determine the degree of particle size sorting, mode of transportation and storage. All these are intended determining the eventual economic potential, highlighting as much as possible the possible sources and their reconstruction.

## ACKNOWLEDGEMENTS

Firstly I wish to sincerely thanks to my coordinator Prof. dr. Ovidiu Gabriel Iancu for ongoing guidance, support and encouragement throughout the period of training and elaboration of the thesis. I also express gratitude to Prof. dr. Nicolae Buzgar, Lect. dr. Dumitru Bulgariu and Lect. dr. Mitica Pintilei for professional help and advice and for the acceptance to be part of the guidance committee established under current legislation (HG 681/2011). Sincerely thanks the distinguished members of the external review committee, consisting of: Prof. dr. Calin Baciu, Prof. dr. Gheorghe Stefan Damian, Lect. Dr. Gheorge Jigău for their patience in reading written materials, suggestions and criticisms offered.

Also express my special gratitude to the teaching staff of the Geology Departament from the Geography and Geology Faculty of "Alexandru Ioan Cuza" University of Iasi, were I found a suitable environment to achieve this work, for encourage and support throughout the preparation of the thesis.

Sincere thanks and great gratitude to Prof. dr. Ryszard Kryza alongside the team from Geological Institute of the University of Wroclaw, Poland, especially Mr. Jacek Ćwiąkalski and Paweł Matz, for the kindness and technical support with electronic microprobe analyzes, the achievement of the thin sections and mineralogical identifications, without this thesis could not be carried out.

I wish to thank in particular to researcher dr. Ciprian Popa and to the entire staff of the Capodimonte Astronomical Observatory of Naples, Italy, for their assistance in sample preparation and facilitation of IR and SEM analysis, during my journey to Naples.

Also sincere thanks to Prof. dr. Ioan Sandu and Mrs. dr. Viorica Vasilache for the kindness and unconditionally support in electronic microscope analyzes within the Arheoinvest Platform (Alexadru Ioan Cuza University of Iasi).

Address, equally sincere thanks to Assist. dr. Valentin Nica and to the technician Sorin Sinca from the Department of Physics, Alexandru Ioan Cuza University of Iasi, for X-ray analyzes (powder method).

I also express gratitude to the engineer dr. Ramona Huzum for constructive discussions, exchange of the scientific materials and for the support and encouragement offered.

I extend thanks due to all those who, professionally, directly or indirectly, through discussions and suggestions offered, contributed to the development of this thesis.

The thesis is divided into 11 chapters that outlines successively achieve the objectives, defining themes and analytical techniques, presentation and description of results and last but not least their interpretation.

**Chapter I** defines the geomorphology and geology of the Bistrita Aurie, Dorna and Neagra Şarului rivers. So are brought details about location, relief, hydrography, geomorphological elements and it is presented in detail the geological context for each river drainage basin.

**Chapter II** presents the history of research carried out in the study area. Also the dealt subject is placed in the current state of knowledge both internationally and nationally, with chronologically specific examples of scientific works, who study different types of heavy minerals in sediments.

**Chapter III** details the analytical methods used in the study. So, is presented in detail the methods of sampling and sample preparation, analytical techniques used and working conditions for each method.

So, samples have been taken at regular intervals taking into account the changes in lithology, facies, texture, flow regime, bed configuration and the availability of field. Were established optimal analytical methods for each type of sample, both in terms of cost and accuracy of the results. The sampling and the analyzing methods used in this study are: the gravity concentration in a gold pan, size sieving, heavy liquid and electro-magnetic separations, optical measurements, electron microprobe determinations, SEM analysis, IR spectroscopy and determinations using X-ray diffractometer (powder method).

## Chapter IV. PARTICLE SIZE ANALYSIS OF ALLUVIAL SEDIMENTS

For statistical data processing of the grain size distribution from Bistrita Aurie, Dorna and Bistrita Neagra Şarului alluvial sediments was used both graphical method and method of moments, which allowed the characterization of grain size distribution. Thus, for each sample separately, was aimed specifically: frequency polygon, cumulative curve diagram and graphic parameters [Mean (Mz), standard deviation (σ), skewness (Sk) and kurtosis (K)].

Sediments smaller than 2 mm from these three rivers and from Bistrița River upstream of the town Rusca are constituted mostly by sand (94-99%), with a significantly reduced contribution by silt (1-6%). The sands are represented in majority by coarse and medium fractions, and rarely very coarse fractions (Fig. 1). Only two samples from the river Bistrita Aurie are composed mainly by fine sands. There is no major difference between alluvial sediments grain distribution of those 4 rivers under study. Average grain size data, highlight the mean (Mz), come to reinforce this. So the average particle size is distributed almost equally between medium and coarse fraction of the alluvial sands.

The values of the standard deviation (σ) indicate for the alluvial sands of the Bistrita Aurie River, a sorting predominantly weak to moderate. So 11 of the samples are poorly sorted, and 6 show a moderate sorting. Dorna and Neagra Sarului river sediments are poorly sorted, while those from Bistrița Aurie have mostly moderate degree of sorting. This indicates the presence of immature sediment. The sediments of the all samples show an asymmetry both moderate as well as sharp with an excess of a fine material.

Sediments with a unimodal distribution have a kurtosis (K) with values that indicate leptokurtic, mesokurtic and platykurtic curves, denoting the existence of several possible sources for alluvial sands. For each of the collected samples from alluvial sediments of the Bistrita Aurie River, the cumulative curve was drawn in order to highlight the grain size populations and the types of transport and deposition. Thus, it was revealed that the sediments are transported mainly by saltation, indicating the existence of a bottom current, quite powerful. However, the turbulence of the rivers in question shows large variations.

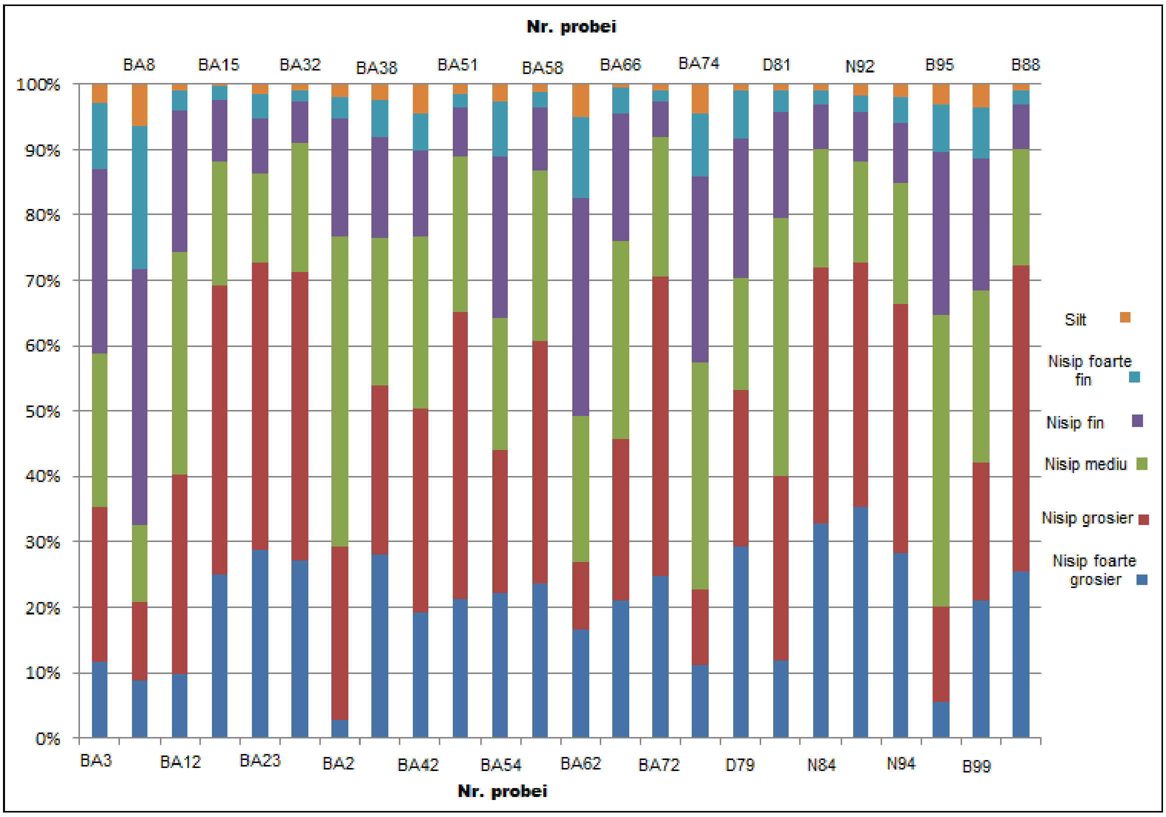


Fig. 1 The granulometry of the alluvial sediments from Bistrița Aurie(BA), Dorna (D), Negra Șarului (N) and Bistrița (B).

## Chapter V. THE DISTRIBUTION OF HEAVY MINERALS FROM BISTRIȚA AURIE, DORNA, NEAGRA ȘARULUI RIVER DRAINAGE BASINS

This chapter presents the main heavy minerals from alluvial sediments, the frequency and the average of each mineral species. Also, the results are highlighted by using different types of separation: gravity concentration in a gold pan, heavy liquid separation and mineralogy identification by electro-magnetic separation.

### V.1 Frequency of heavy mineral from alluvial concentrates

For the determination of heavy mineral frequencies, the method of counting grains according to Luepke (1985), in which more than 200 grains per sample should be identified. Dryden argues that the probable error in the mineral counting shall not be more than 5%. To define accuracy, the probable error (p.e.) of counting n grains in each mineral species was calculated using the following formula:

$$\textbf{p.e.}\text{ (in no. of grains)} = 0.6745\sqrt{\boldsymbol{npq}},$$

where **n** is the total number of grains identified, **p** is the probability (chance that any grain in the slide will belong to a certain specie) and **q** is the chance that any grain will not belong to such a category (Luepke, 1985).

Using these data, was performed a map of the researched area (Fig. 2) in which was projected the frequency of heavy minerals from representative alluvial concentrates in order to provide an overview of their differences in distribution.

The study area was divided into three sub-areas/hydrographic basins, depending on the quantitative participation of major heavy minerals, as follows: (1) the Bistrița Aurie upper basin, upstream of the town Cârlibaba, (2) the Bistrița Aurie lower basin, upstream of Vatra Dornei, (3) the Dorna basin and (4) Neagra Șarului basin.

In the hydrographic basins of these three studied rivers are described following minerals: garnet, clinopyroxene, manganese oxides, magnetite, maghemite, titanomaghemite, iron oxides, titanium oxides, ilmenite, chlorite, chloritoid, pyrite, apatite, zircon, monazite, epidote , hypersten, biotite, muscovite, etc.

The alluvial sediments from the Bistrița Aurie upper basin are characterized by the abundance of garnets which vary between 79.71 (± 1.33) % and 64.11 (± 1.47) % of the total heavy mineral concentrate. The alluvial deposits of the Bistrița lower basin record a noticeable enrichment in manganese oxides (min. 2.11 (± 1.05) %, max. 23.82 (± 1.55) %) (Ciortescu et al., 2014b).

In the hydrographic basins of Neagra Șarului River, the heavy minerals with highest abundance are pyroxene (min. 19.46 (± 1.35) %, max. 25.26 (± 1.48) %), manganese oxides and sometimes pyrite. In terms of typology and abundances of the heavy minerals, Dorna River can be considered an intermediate zone. The sediments of this river are a mixture of minerals that can be found both on the Bistrita River Valley and the Neagra Șarului River. Thus, among the main minerals whose abundances are similar, we can mention: garnet, pyroxene, manganese oxides, iron oxides and pyrite.

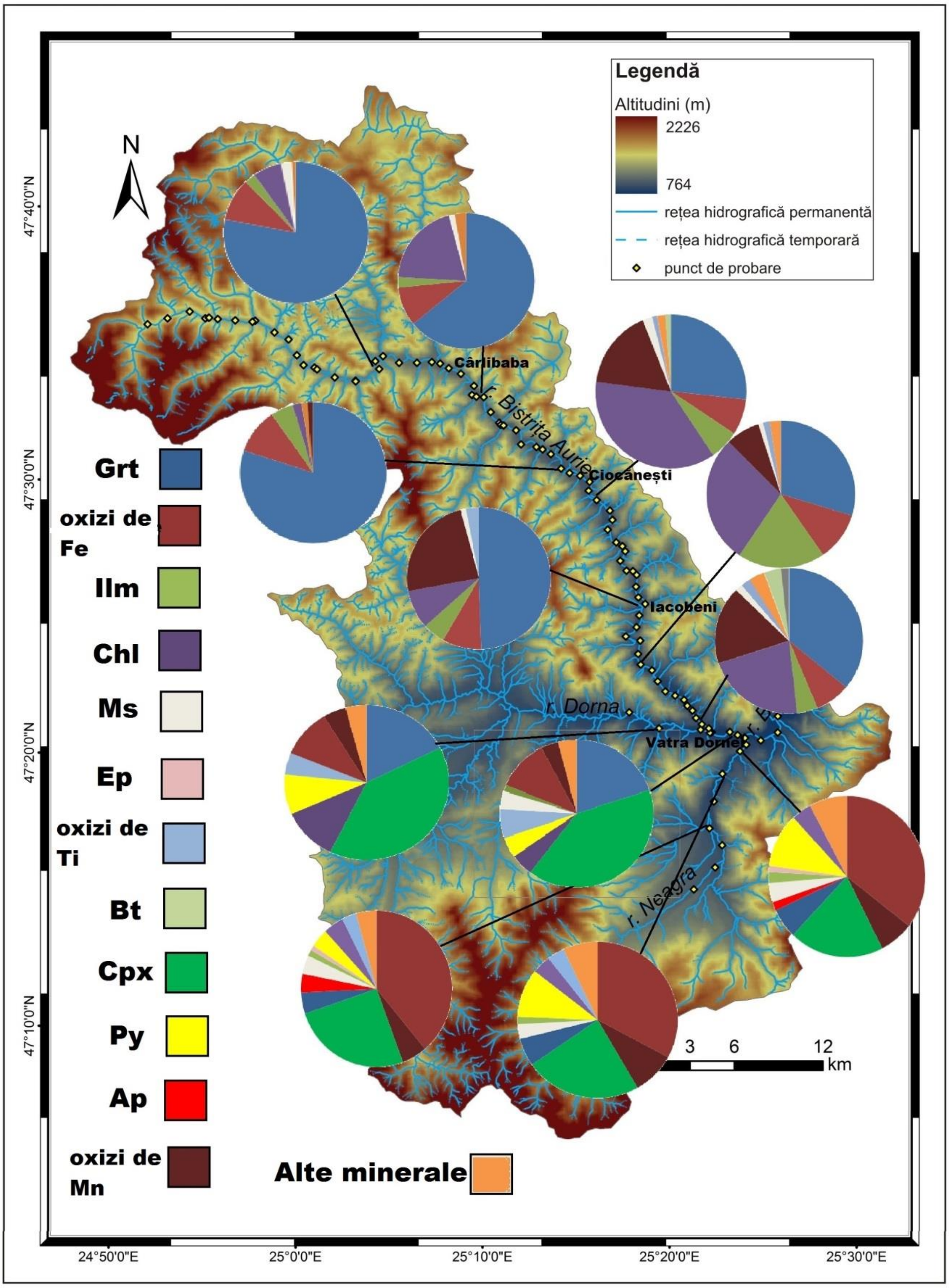


Fig. 2 Map of the Bistrița Aurie, Dorna and Neagra Șarului rivers drainage basins, showing the sample location and the frequency of major heavy minerals from representative alluvial concentrates.

### V.2 Heavy liquid separation of heavy minerals

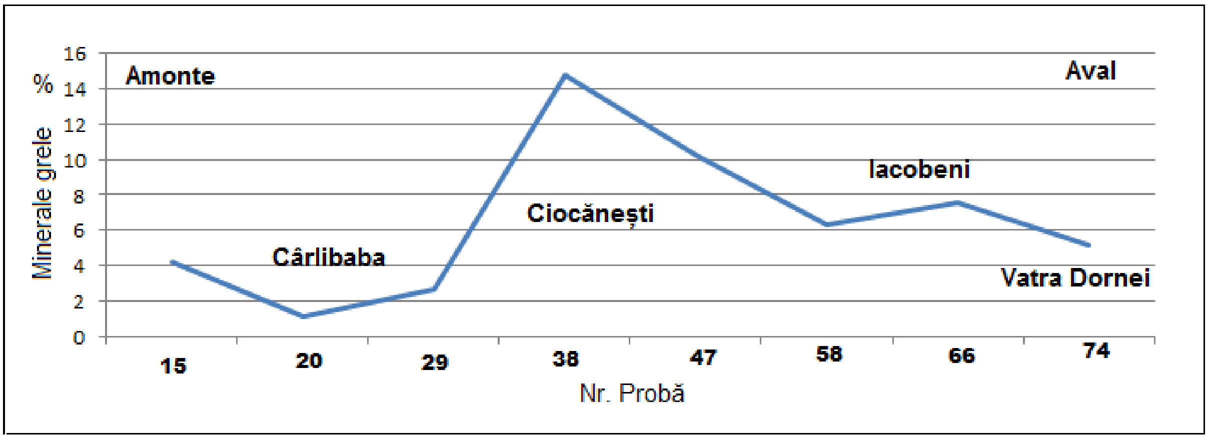


Fig. 3 Average distribution of heavy minerals from the alluvial sediments of the Bistrița Aurie River, upstream to downstream.

Alluvial samples separated using heavy liquid, revealed considerable variation in terms of the concentration of heavy minerals, which are recorded both in the Bistrița Aurie River (upstream to downstream) and among these three studied rivers.

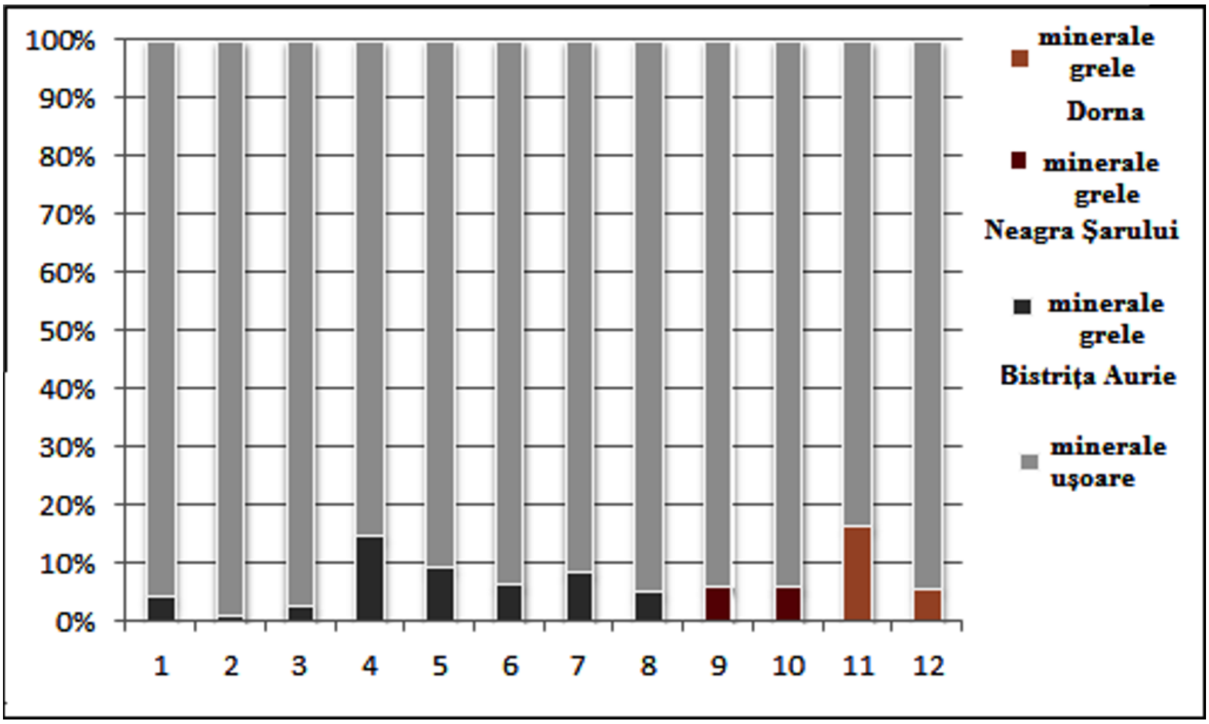


Fig. 4 Distribution of heavy and light minerals in alluvial representative samples from Bistrița Aurie, Dorna and Neagra Șarului rivers.

The total amount of heavy minerals from the total of alluvial minerals from Bistrița River, expressed as a average, vary significantly from upstream to downstream (Fig. 3). Thus, samples with the lowest content of heavy minerals were collected upstream (1.5%), near the springs. They are experiencing a significant increase near the Ciocănești Town, thereby reaching content up to 15% of heavy mineral, followed by a decrease in content, up to 8% near the Iacobeni Town and 5% near Iacobeni.

The sample with the highest content of heavy minerals was collected from the alluvial cone of the Dorna River (Fig. 4).

Unlike the other two rivers alluvial deposits, Negrei Şarului alluvial sediments have a significantly lower content of heavy minerals.

### V.3 Electromagnetic separation of heavy minerals

Approximately 1.2 g of sample from the alluvial concentrates were subjected to separation on a current strength increasing from 0.5 to 0.5 A. Previously, by mass of samples subjected to this process, ferromagnetic minerals were removed using a magnet. For electro-magnetic separation of minerals from alluvial sediments of the river Bistrita Aurie, Dorna and Black Şarului the $15^0$ slope have been used, because the $20^0$ one, provided a separation with not a high accuracy. At this stage of the work it was intended magnetic separation of heavy minerals, the major constituent of the alluvial sediments from the areas of interest. Thus, for each separated mineral species from alluvial concentrates researched in this study was determined by a range of separation depending of the current intensity, compared with those from the literature, in order to determine the heavy minerals and the differences between their provenances (Fig. 5).

Regarding the mineral species from Bistrița Aurie, Dorna and Neagra Șarului alluvial sediments can be assert the following:

- The separation intervals of the garnet varieties correspond mainly to the almandine, followed by andradite and grossular varieties;

- The garnets from Bistrița Aurie District upstream of Ciocăneşti are similar to those from downstream, differing only in terms of optimal range, which indicates an additional source for to those mentioned above;

- The current intensity ranges, in case of garnet separation are extending to 0.45 A, sometimes up to 0.5 A, for Dorna and Neagra sediments. Thus, in these areas there is a variety of red garnet, which is missing from the Bistrița Aurie sediments;

- An interesting aspect, specific to study areas is the presence of ferromagnetic garnet. It was separately both with magnetite, as well as at the low current intensities.

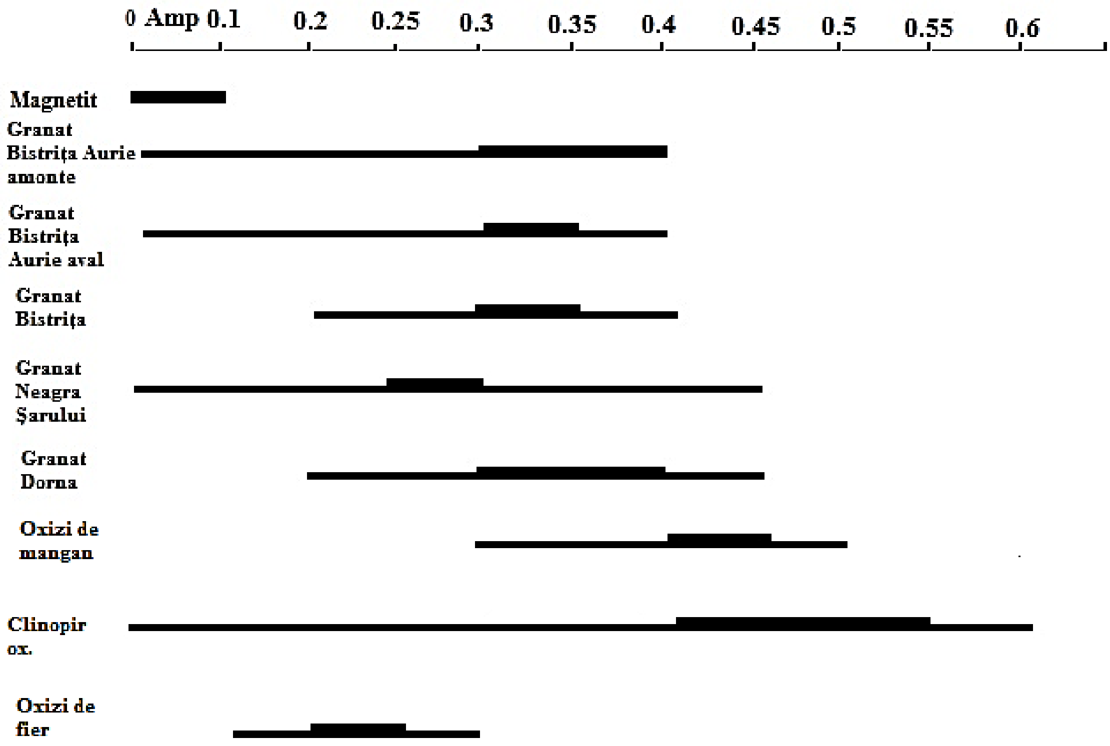


Fig. 5 Magnetic susceptibility of the heavy minerals from Bistrița Aurie, Dorna and Neagra Șarului alluvial sediments, with a $15^0$ slope, depending of the current intensity (A); Thin lines represent current intensity intervals where each mineral species was separated, bold lines represent the optimal separating range.

The fact that these minerals exceed the ranges of separation present in the literature can be considered an anomaly, most likely due to rich inclusions titano-magnetite and magnetite. This can be noted in the case of clinopyroxene group;

- The clinopyroxenes are separated at rages belonging to feroaugite, hedenbergite, diopside, but the optimum intervals correspond to augite;
- The manganese oxides have been separated only from 0.5 mm and 0.125 mm grain fractions. This indicates the lack of manganese grains from in the lower fractions, most likely due to the high susceptibility to alteration, friability and increased solubility. It could be also a factor that depends on the initial size of the grains from the source areas. Due to an extremely large variety of manganese oxides, magnetic separation is insufficient metod to determine their varieties.

## Chapter VI. STUDY OF GARNETS FROM BISTRIȚA AURIE, DORNA, NEAGRA ȘARULUI RIVER SEDIMENTS

### VI.1 The distribution of garnets from Bistrița Aurie river basin

Garnet is the most abundant heavy mineral in the Bistrița Aurie alluvial deposits, especially in the upper basin located upstream of Ciocănești Town, where it reaches 79.71 (±

1.33) % (Ciortescu et al., 2014b). The form of the grains of this mineral range from very angular to rounded. Some of them preserve a subhedral habit; others are just angular fragments, resulting from transportation and influence of hydraulic factors. Garnet colour ranges from pink to purple in samples from upstream of Ciocănești, and pink to purple and orange, downstream of that region (Fig. 6). EDS spectra of garnet from the Bistrița Aurie alluvial deposits highlight four distinct varieties (Fig. 4): almandine-rich (Fig. 4 E), almandine with subordinate grossular (A), grossular-almandine-spessartine (C), and grossular-andradite. Also, to a lesser extent, a variety with almandine and pyrope end-members has been identified. These varieties are specific to low- and medium-grade metamorphic rocks Ciortescu et al., 2014b).

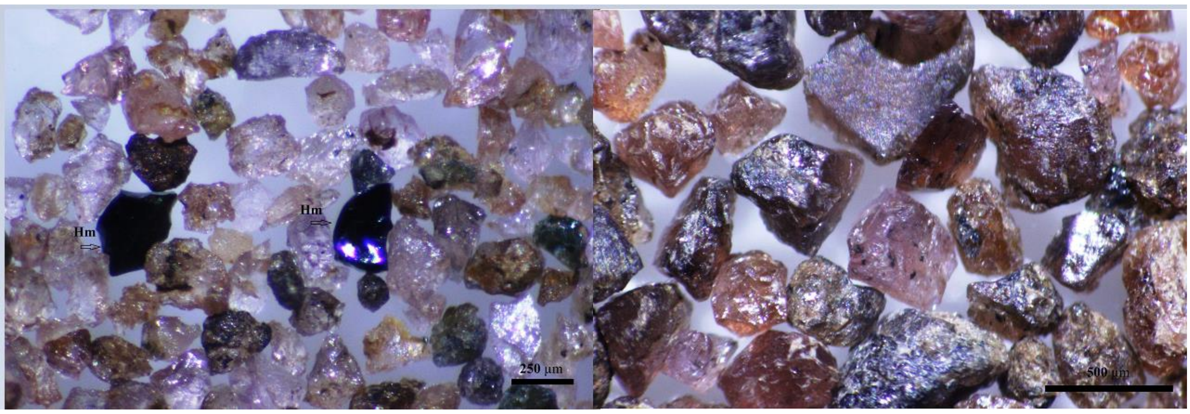


Fig. 6 Garnet crystals from the alluvial deposits of the Bistrița Aurie River (Ciortescu et al., 2014b).

## VI.2 The distribution of garnets from Dorna river basin

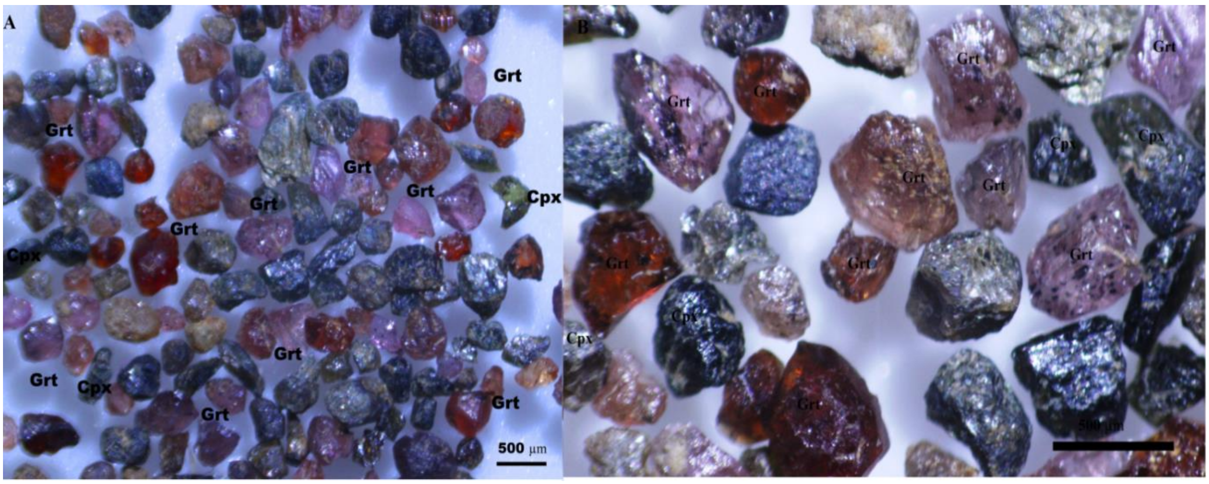


Fig. 7 Garnet crystals from the alluvial deposits of the Dorna River (Ciortescu et al., 2014b).

Garnet in the Dorna River alluvial sediments appears in all samples, in amount ranging from 17.59 (± 1.14) % to 19.82 (± 1.30) %. Shapes and colours of the garnet from this area are similar to those in the Bistrița Aurie garnets. However, a specific feature of the sediment from the Dorna River is occasionally found bright red garnet (Fig. 7 A și B), which has been separated at intensities of current ranging from 0.35-0.45 A, unlike the pink garnets separated from at the lower intensity.

### VI. 3 The distribution of garnets from Neagra Șarului river basin

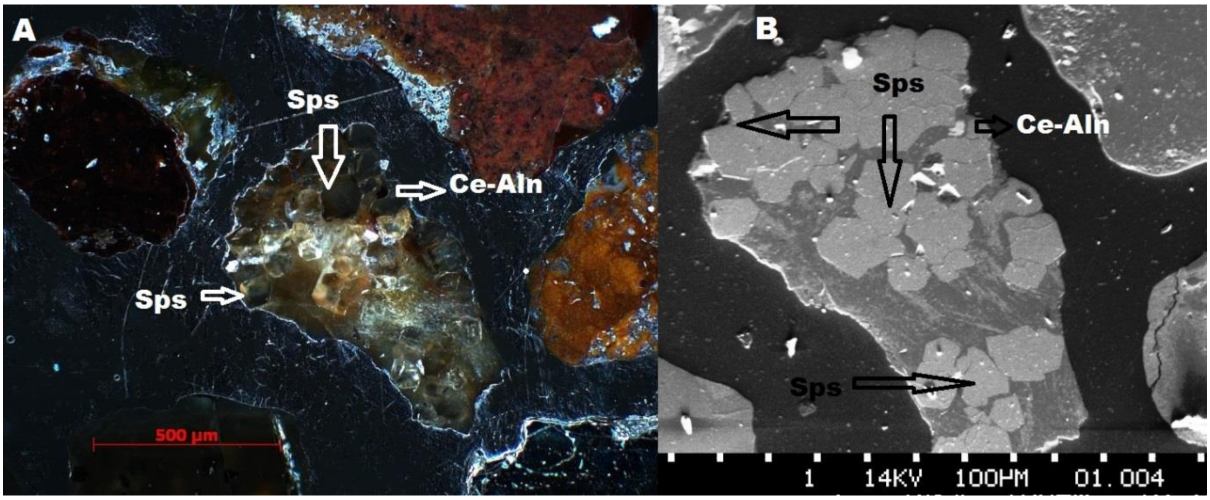


Fig. 8 Photos of a aggregate with spessartine and Ce-allanite; A- polarizing microscope image; B- BSE image (backscatter electron image) (Ciortescu et al., 2014).

Garnet, ranging from pink, red to brown, with a low participation, between 4.33 (± 0.69) and 6.08 (± 0.85) %, occurs in all samples collected from the Neagra Șarului river basin except the sample collect from the Haitei stream. The crystals occur as irregular grains, angular, with conchoidal fracture (Ciortescu et al., 2014). Frequently, the crystals are transparent or translucent do the numerous inclusions. In a sample collected from the alluvial cone of the river could be described an aggregate composed by isometric crystals of spessartine, quartz and Ce-allanite (Fig. 8 A and B).

### VI. 4 Geochemistry of garnets

All the analysed garnet grains from the alluvial sediments of Bistrița Aurie River represent a chemical mixture of the components: almandine (Al), pyrope (Py), spessartine (Sps) and grossular (Grs). Their chemical compositions are plotted in two types of diagram:

1. Almandine-pyrope-spessartine
2. Pyrope (XMg), almandine + spessartine (XFeMn) and grossular (XCa).

Both types of charts are used to display grades of regional metamorphism and to give clues about genesis of the garnet.

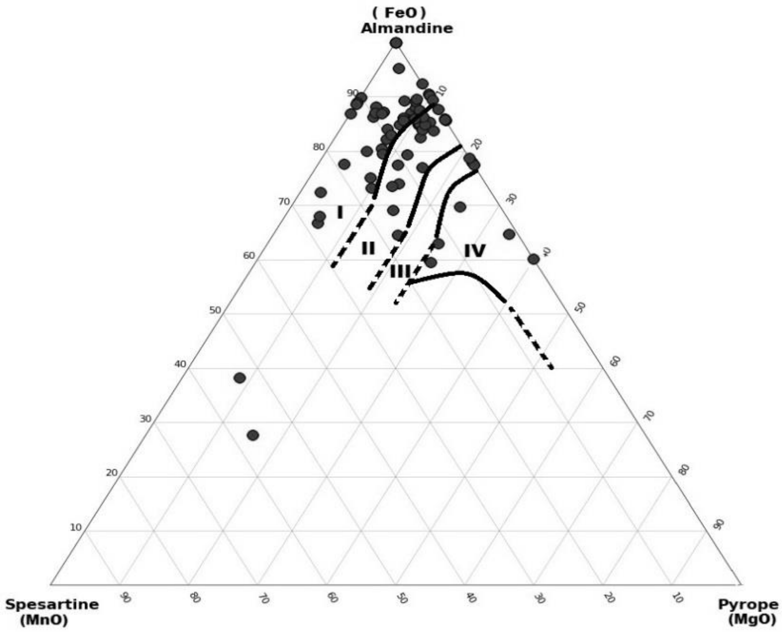


Fig. 9 Chemical composition of the detrital garnets from the alluvial sediments of the Bistrița Aurie River in FeO-MgO-MnO ternary diagrams. The individual fields represent various metamorphic zones (modified after Aubrecht & Meres, 2000). I - low grade metamorphic conditions (greenschist facies), II - low to medium grade metamorphic conditions (low - temperature amphibolite facies), III - medium grade (amphibolite facies) and IV - high grade (granulite facies) (Ciortescu et al., 2014d).

According to the chemical composition, garnets from alluvial deposits can be divided in four groups with different sources. The first one is rich in almandine and (more than 75 %) have a low content of grossular or spessartine and pyrope. This type of garnet can be found in compositional group no. 3, in the compositional field B (Fig. 10), and in the field I and II of the Py-Sps-Al diagram. Also, they can be found as a major component in all the samples collected along Bistrița Aurie River.

The second one has a high almandine component, moderate grossular (15-30 %), and low pyrope. This group can be found in compositional group no. 4 and in the compositional field B (Fig. 4) and consists in garnets from felsic amphibolite that either have a more Ca-rich or more intermediate composition. It may also be found in all the collected samples, especially in the lower part of the hydrographic basin, samples no. 7 and 8 (Fig. 11). These two groups have, as source, low and medium metamorphic rocks from the Bretila and Rebra Metamorphic Units belonging to The Crystalline-Mesozoic Zone. Not very frequent, the third group has a high spessartine (25-60 %), moderate almandine and very low pyrope. This can be seen in the the field I and II of the Py-Sps-Al diagram, which means it had grown under low to medium grade metamorphic conditions. The sources of this group are the low grade metamorphic rocks from Tulghes Metamorphic Unit (Ciortescu et al., 2014d).

The most problematic were few garnet grains with high content in pyrope component (from 25 to 40%) and low grossular. This type of garnets, belonging to the 4th group, is believed to be derived from high-grade rocks. High content of pyrope component in these garnets indicates that their source rocks have granulitic character. This group of garnets can be seen, classified according to the Py-Sps-Al diagram, in the field IV (Fig. 9) which reinforces the idea that the most probable source for this group of garnets has been metamorphosed under high metamorphic condition. This group can also be found in compositional group no. 2 and in the compositional field A. Garnets in group 2 derive from felsic granulite rocks (all source rocks with a pelitic, semipelitic, meta-sedimentary), type A garnet (low Ca, high Mg) being typical for high-grade meta-sedimentary rocks (granulite facies) with a forming temperature greater than 700oC (Keulen et al. 2012). From the regional point of view, the source is not very clear because in the hydrographic basin of the Bistrița Aurie metamorphic formations with such a high content of pyrope have not been described thus far (Ciortescu et al., 2014d).

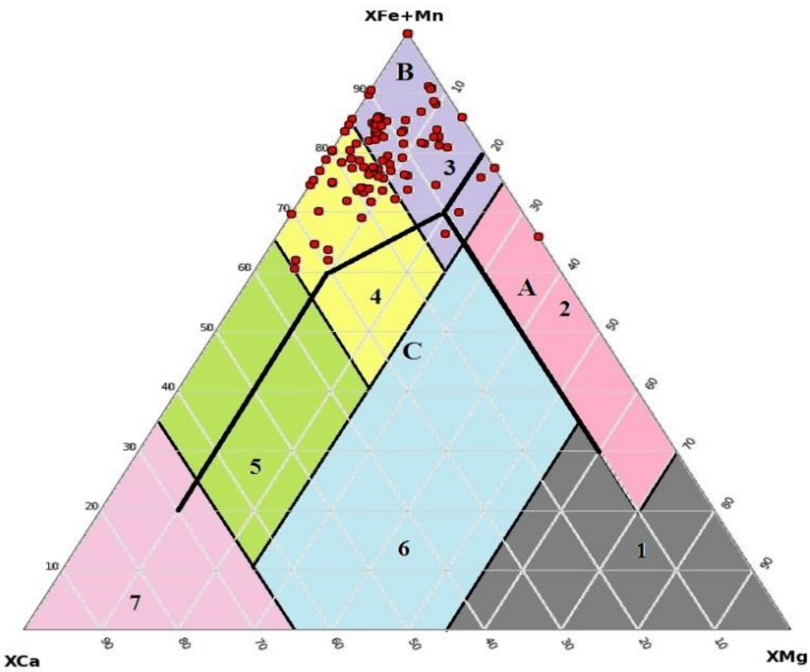


Fig. 10 Ternary diagram showing the distribution of garnets from Bistrița Aurie River in seven compositional groups and compositional fields for Type A, B and C. Garnet analyses are plotted by their end-member compositions pyrope (XMg), almandine + spessartine (XFeMn) and grossular (XCa) (modified after Keulen et al. 2012). (Ciortescu et al., 2014d).

Instead, Balintoni & Chițimuș (1973) assumed for the Tulgheș Unit the presence of a metamorphic event with higher intensity than the one currently accepted. Also, Hîrtopanu (2004) suggests the existence of five different metamorphic events in the metamorphic history of the Tulgheș Unit.

The 4th garnet group depicted in this study may be formed under metamorphic conditions similar to metamorphic event no. 2 (M2). During this event, the temperature exceeds 700$^{o}$ C and the mineralogical assemblages from Tulgheș Unit underwent an isothermal decompression and a widespread amphibolite to granulite facies overprinted. Since the garnets with high pyrope content have been sampled only from sites situated upstream of Ciocănești, the source is located in the upper part of the Bistrița Aurie upper basin (Ciortescu et al., 2014d).

**VI. 5 Mineral inclusions**

Very often, this group of minerals has forms which vary from very angular to angular (Fig. 11A). Rarely could it be observed the rounded form. The crystals are translucent to transparent. Very often, it can be observed different types of solid inclusions (Fig. 11B): opaque, fibrous and acicular.

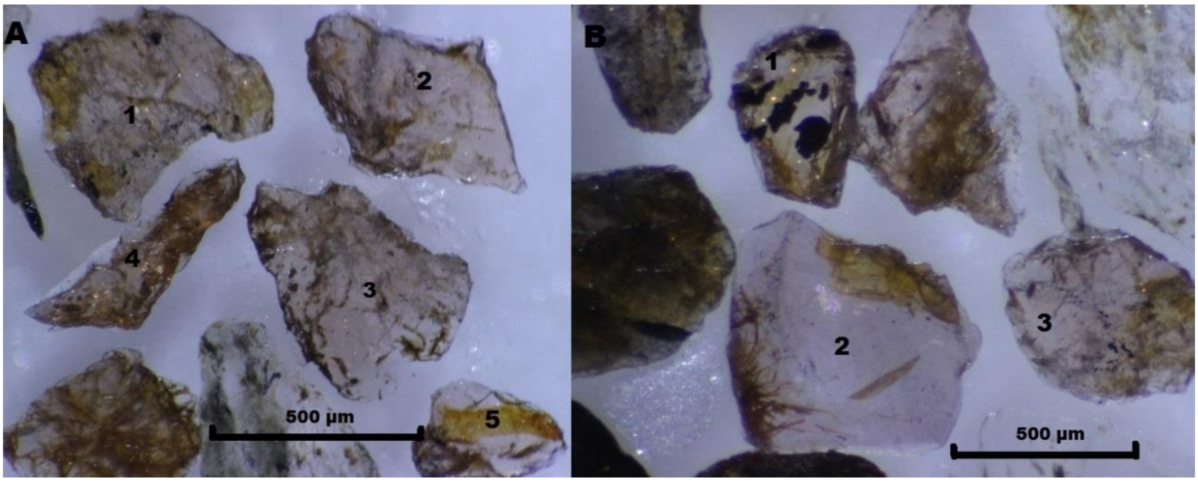


Fig. 11 Garnet crystals in thin sections, image captured by stereo microscope; A- Variation of garnet forms: very angular (2 and 4), angular (1 and 3), rounded (5); B- Type of inclusions in garnets: opaque inclusions (1), fibrous and acicular inclusions (2), opaque and acicular inclusions (3) (Ciortescu et al., 2014d).

Also in terms of mineralogy, the detrital garnets from Bistrița Aurie sediments show a wide range of solid inclusions as quartz, ilmenite, hematite, apatite, rutile, titanite, zircon, monazite, graphite, Ce-allanite etc.

## VI. 6 The economic potential of garnets

Globally, industrial garnet is marketed and used for industrial purposes as abrasive material (blasting agent), water jet cutting, applied abrasive products, slurry and abrasive powder, for cleaning and filtering water, etc.

Specifications met by alluvial garnets according to the reference values (Elsner, 2010) of the studied the rivers, as industrial garnets, are mostly met.

First of all, hardness and dynamic viscosity of the material used industrially for the purposes mentioned above must be as high as possible. For this reason it is considered ideal almandine (Elsner, 2010). In this case, over 95% of the analyzed garnet grains belong to the almandine variety. Also, the granules of the study area do not have many fractures, and mineral inclusions have a moderate abundance. Alluvial concentrates do not have radioactive minerals. Also, garnets can be found in all grain size fractions, and they are not affected by the alteration. Furthermore, the crystal form varies from angular to rounded.

Industrial garnets are extracted both from placies deposits (alluvial garnet) as well as source rock (crushed garnet). In this case, silt can be exploited more easily, and besides garnet there can be extracted in various amounts other economically valuable minerals: ilmenite, rutile or zircon. Also, there are no qualitative differences between the two types of deposits (Elsner, 2010). Benchmarks that must be met for a garnet deposit to be exploited are related to the percentage of heavy mineral sand deposits (mass%), the garnet percentage of concentrate alluvial (% by mass) and total reserves of garnet (in kilotonnes) (Elsner, 2010).

In the present study, only two of the three benchmarks were followed. The last of them, namely the total reserves of garnet (in kilotonnes) is quite difficult to achieve. Thus, assessment of the garnets economic potential from Dorna and Bistrița Aurie rivers alluvial deposits is limited.

Therefore, the percentage of heavy mineral from sand deposits must not be less than 4%. Of all the samples from the alluvial deposits of the rivers Dorna and Bistrița Aurie only those collected from the upper section of the river Bistrţa Aurie, upstream of Ciocăneşti, are not within the standards required (Fig. 3). They have an average of 2% heavy minerals. In contrast, in Ciocăneşti zone and the alluvial cone of river Dorna, the total heavy minerals is 15 and 17% (Fig. 4). However, these areas have a garnet concentration of 80%, respectively 20%, of all minerals in alluvial concentrates. All these correspond exactly to the reference values mentioned above and increase the amount of economic potential.

## Chapter VII. STUDY OF TITANIUM OXIDES FROM BISTRIȚA AURIE, DORNA, NEAGRA ȘARULUI RIVER SEDIMENTS

The principal sources of Ti, used on a large-scale in industry, are the following minerals: ilmenite, leucoxene, and rutile (Keulen et al., 2012). One of the most essential parameter to the assessment of quality and economics of a potential deposit is the determination of the TiO2 average content of the Ti minerals that must exceed 53 % $TiO_2$ (Elsner, 2010).

Classification of titanium minerals from the hydrographic basin of the studied rivers is based on the chemical composition of the detrital grains. So $TiO_2$ polymorphs (rutile, anatase and brookite) could not be distinguished and are grouped as a single mineral species (rutile). The distinction between ilmenite, leucoxene and rutile is entirely based on the proportion of $TiO_2$. Therefore, the classification scheme of the titanium minerals in this study is the following:

- magnetite <21% TiO2 <Ti-magnetite <46% TiO2 <ilmenite <70% TiO2 <leucoxene <87.5% TiO2 <rutile (Keulen et al., 2012).

The titanium oxides have been described in all the analyzed samples both as individual grains and as inclusions in others heavy minerals species. So, the titanium mineral species founded in the alluvial concentrates are: rutile, ilmenite, leucoxene, titanite and titano-magnetite. About 40% of ilmenite crystals have a concentration very close or identical to the ideal stochiometric value of 52.6 wt. % (Fig. 12) (Ciortescu et al., 2014a).

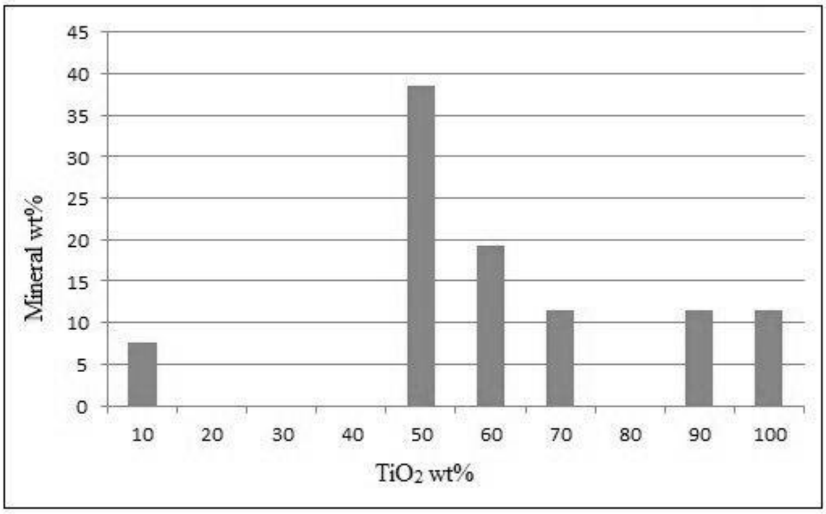


Fig. 12 Average TiO2 content of the Ti mineral fraction in Bistrița Aurie River sediments. (Ciortescu et al., 2014a).

The average TiO2 content, greater than 50 wt. % for more than 90 % of the Ti minerals from the Bistrița Aurie River sediments (Fig. 2), is one of the most essential parameter to the assessment of quality and economics of a potential deposit. This fact increases the potential economic value of the Bistrița Aurie alluvial sediments. Also, this parameter indicate progressive leaching of Fe from primary ilmenite specifically to mature sediments (Babu et al., 2013). In this case, however, we can not talk about maturity of the alluvial sediments, the avarage of TiO2 is strictly dependent by genetic factors involving the source rocks. A proof of this is the ilmenite inclusions in garnet or staurolit, which most of the times the avarage value of $TiO_2$ is greater than 52.6%.

Ilmenite is the most abundant titanium mineral. It varies from 2.44 (± 0.45)% to 19.02 (± 1.22)%. Concentrate with the highest participation was collected near the Iacobeni Town.

The titano-magnetite occurs very rare in the alluvial concentrates because of the pretreatment related by removal of ferromagnetic fraction. (Ciortescu et al., 2014a).

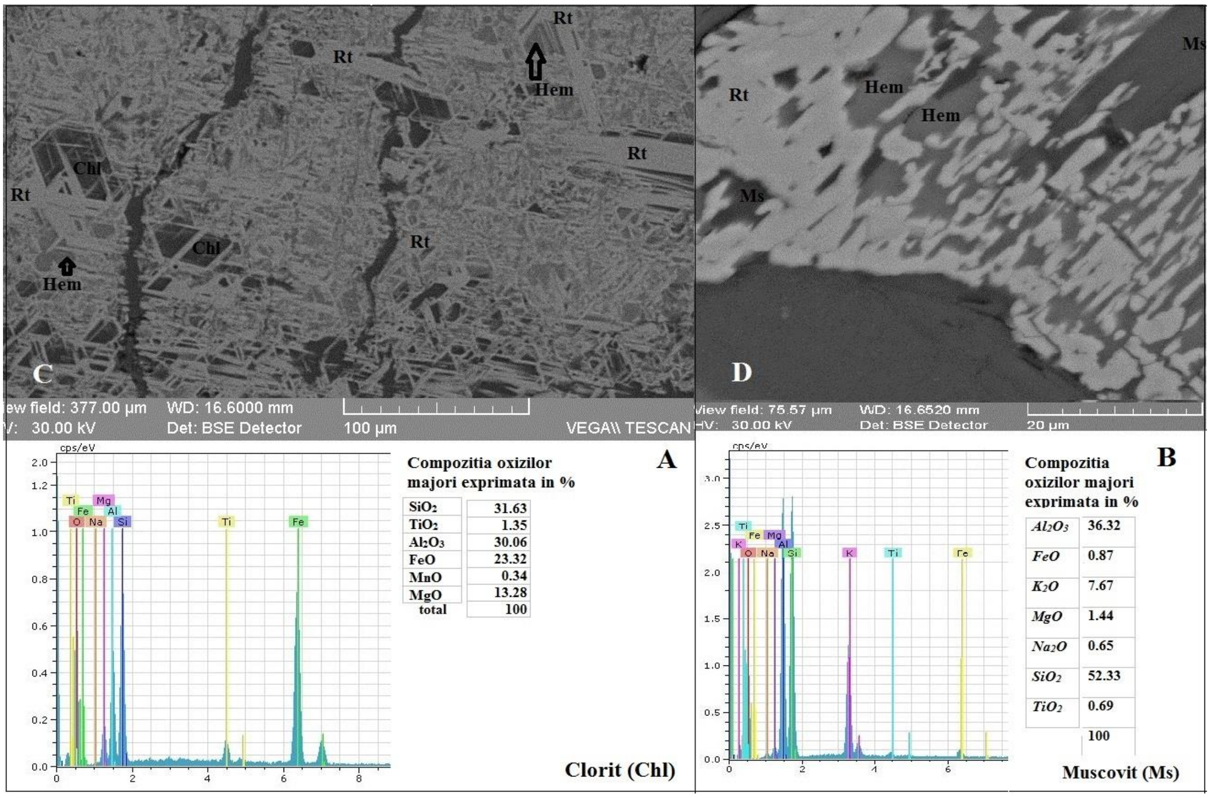


Fig. 13. C – BSE image of a rutile with sagenitic structure (backscatter electron image); D - BSE image of a rutile detrital mineral; A - EDS spectra and the composition of the major oxides of chlorite from sagenitice spaces o the rutile structure; B- EDS spectra and the composition of the major oxides of the muscovite from rutile-hematite-muscovite aggregate.

The rutile crystals that occur in alluvial concentrates show very often a sagenitic structure that forms a network of equilateral triangles or rhomboids. Marginal rutile crystals are smaller and less frequent (Fig. 3C). The remaining free space is occupied by hematite (Fig. 13 A, B, C, D) and chlorite after biotite (Ciortescu et al., 2014a). Such aggregates are described by Balintoni and Chițimuș (1973) as a rutile paramorph after brookite, in the

Tulgheș Metamorphic Unit. These paramorphs are attributed to the initial metamorphosis of Tulgheș unit, and the transformation of biotite to chlorite is hercynian and corresponds to last retrograde metamorphic event (Balintoni and Chițimuș 1973).

## Chapter VIII. STUDY OF IRON AND MANGANESE OXY-HYDROXIDES FROM BISTRIȚA AURIE, DORNA, NEAGRA ȘARULUI RIVER SEDIMENTS

### VIII.1 The distribution of magnetite from alluvial concentrates

The magnetite grains from the study sediments present various forms and roundness. The magnetite grains range from angular to round in shape. In the samples collected from the Bistrița Aurie upper basin, magnetite is very angular to angular (Fig. 14 A). The grains of this mineral become increasingly more rounded as we approach the Vatra Dornei town (downstream) (Fig. 14 D).

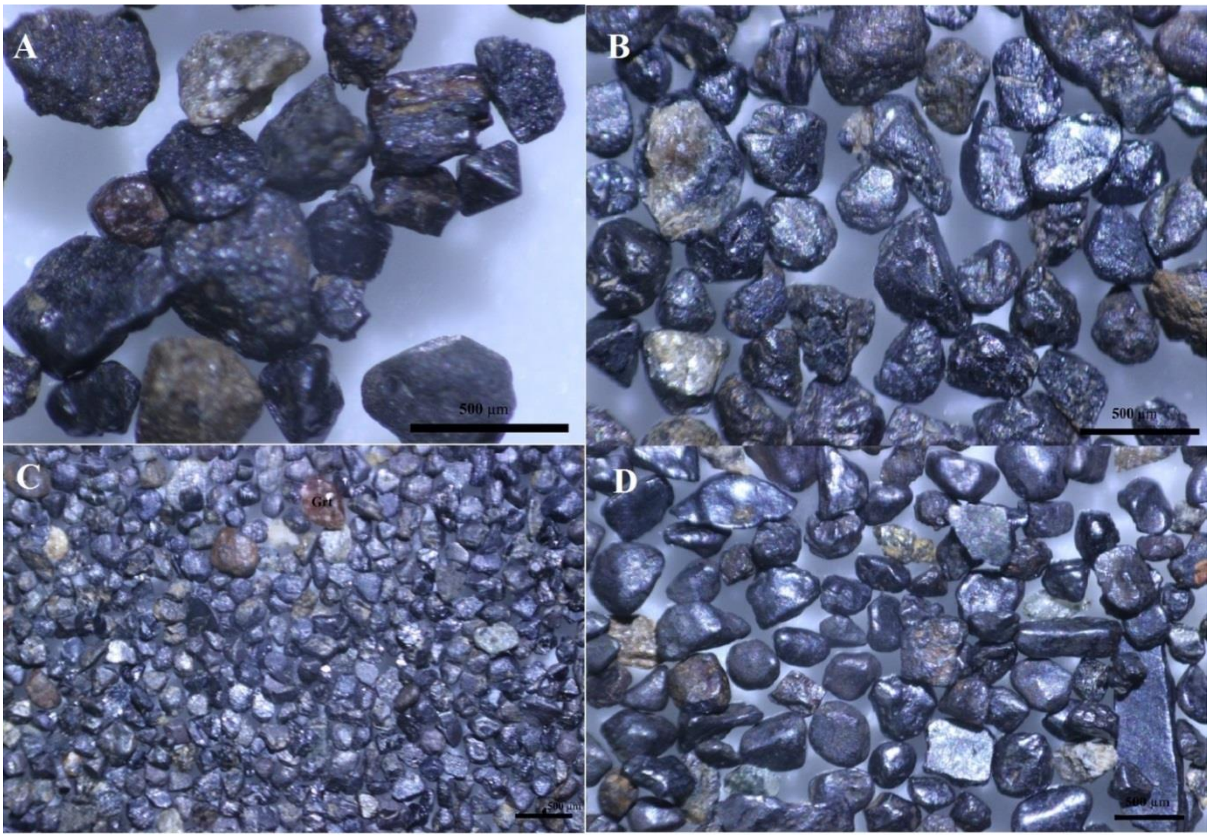


Fig. 14 Magnetite grains with increasing roundness from up- to downstream located sample sites; A - sample collected near the springs of the Bistrița Aurie River; B - sample from Ciocănești town; C - sample from Iacobeni town; D - sample from Vatra Dornei town (Ciortescu et. al. 2014b).

Figure 14 A, B, C, and D show the change from angular to rounded magnetites, when going downstream, that is with increasing distance from the source areas (Mange & Maurer, 1992). This difference is given by the distance that magnetite grains have covered it under the action of hydraulic factors. Magnetite is one of the most abundant opaque heavy mineral present in the research area. The concentrates have magnetite ranges between 6.9 and 12%. The maximum concentration of the magnetite is recorded in the 0.5, 0.25 și 0.125 mm fractions of the alluvial concentrates. The ferromagnetic fractions are generally characterized by dark colors, mainly blackish. But in this case, in all the samples, the color of the magnetite varies from black to grayish and from yellow to brown-reddish. (Ciortescu et. al. 2014e) The variety of colors is due to the presence of alteration crusts on the mineral surfaces, caused by processes such as limonitization (Fig. 15 A și B). The Călimani Complex, an important source for a large part of magnetite, is strongly affected by hydrothermal alteration followed by the physical and chemical weathering, which lead to hematitization and limonitization (Stumbea, 2010).

Another reason for the presence of the crust is the in-situ alteration of magnetite caused by acidic water of the Neagra Șarului River and its tributaries. The water from the river has a pH ranging between 2.3 -4.5, and contains very high sulfur (883 - 1016 mg/l) and iron concentrations (88-222 mg/l) (Ionce, 2010).

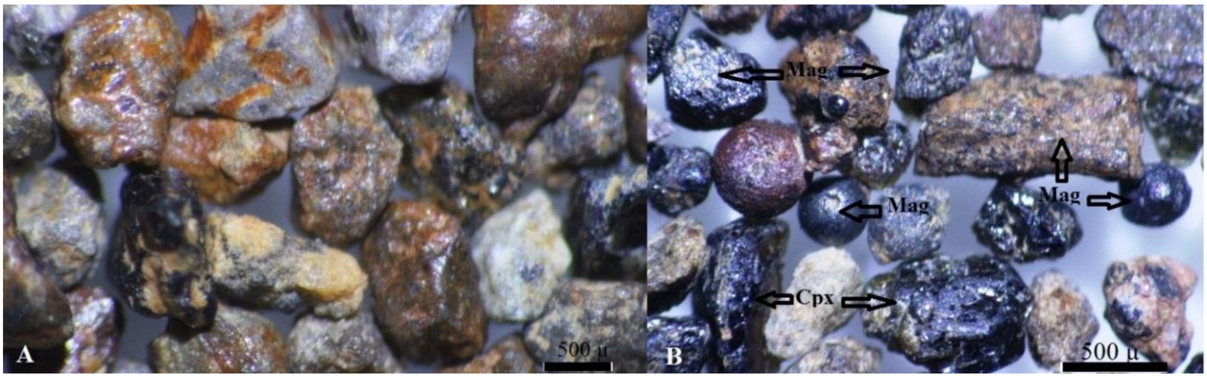


Fig. 15A - Ferromagnetic fraction from the alluvial concentrates of the Neagra Șarului River; B -Various degrees of roudnes and alteration of magnetite fom the Neagra Șarului alluvial deposits (Ciortescu et. al. 2014e).

X-ray diffraction pattern carried out on the ferromagnetic altered fraction of the Neagra Șarului River sediment, indicating the presence of maghemite and titano-maghemite (Fig. 16). Ferromagnetic fraction of Dorna River alluvial deposits is a mixture of features from the other two studied rivers. Thus magnetite were described unaltered crystals, black-gray, like magnetite from alluvial deposits of the Bistriţa Aurie River and magnetite grains with various degrees of alteration with ferromagnetic crystals of pyroxene, specific to Neagra Şarului River sediments. So the magnetite from alluvial deposits of the Dorna River has as a source different types of rock similar to those from the Bistrita Aurie basin and the Neagra Şarului basin.

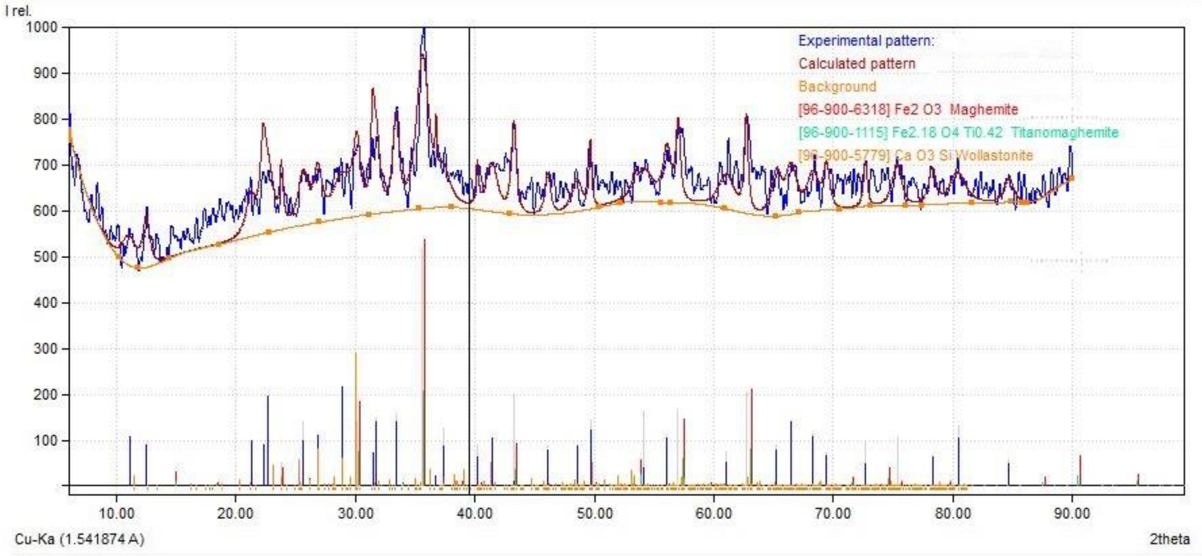


Fig. 16 X-ray diffractogram pattern of the ferromagnetic fraction from alluvial sediments of the Neagra Șarului River; highlights the presence of thr titano-maghemite and maghemite.

## VIII.2 Study of other iron oxy-hydroxides from Bistrița Aurie, Dorna, Neagra Șarului alluvial sediments

Iron oxides and hydroxides are appearing in all the samples collected from Dorna and Bistrita Aurie rivers, including the particle size fractions of 1.6 and 1 mm, with a participation ranging from 6.93 (± 0.8) to 10.68 (± 0.96)%. According to the EDS spectra, the main oxide which occurs in river sediments is hematite. It is commonly found as inclusions in other heavy mineral from alluvial concentrates. Form aggregates with ilmenite, manganese oxides and various light mineral (Ciortescu et al., 2014b). Iron oxides and hydroxides occur in all samples of Neagra Şarului alluvial sediments, with a participation ranging from 22.91 (± 1.58) to 38.52 (± 1.65) %. The crystals generally range from black to dark brown. Also, in the analyzed samples, have been identified iron carbonates, such as Mg-Ca siderite and ankerite (Ciortescu et al. 2014).

## VIII. 3 Study of manganese oxy-hydroxides from Bistrița Aurie, Dorna, Neagra Șarului river sediments

Manganese oxides are missing in some samples collected from the district upstream of Ciocăneşti town, but progressively increase, up to 23.82 (± 1.56)%, while advancing towards this town. Also, they are the main heavy mineral in the alluvial sediment downstream of Ciocăneşti. These oxides were concentrated in the 0.5-1.6 mm range. In the grain fractions below 0.25 mm, the manganese oxides disappear (Ciortescu, 2014b).

This group of minerals presents rounded to very rounded shape and they are blackish, brownish and sometime with a bluish tint (Fig. 17).

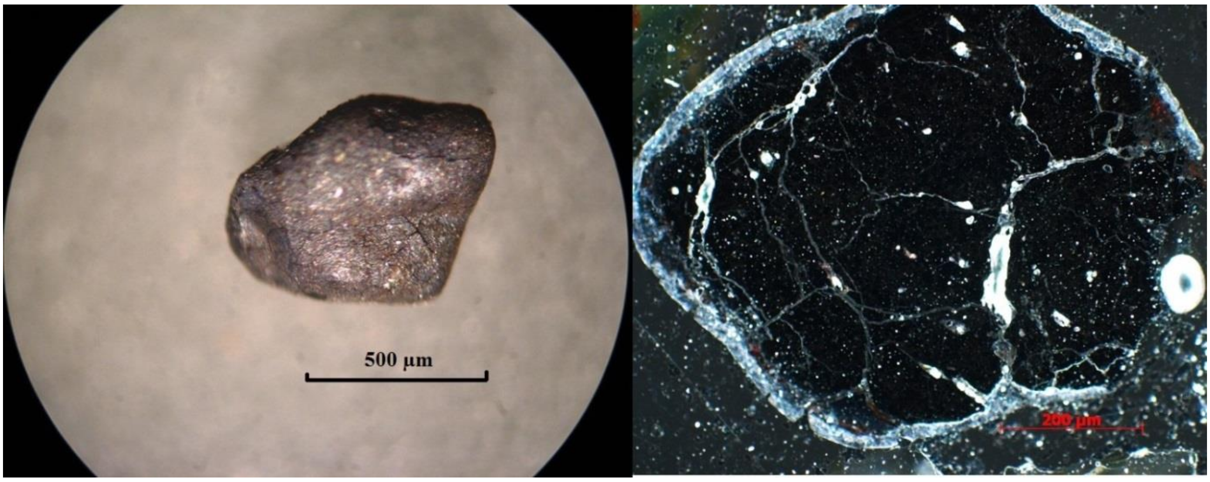


Fig. 17 Manganese oxide detrital grain from Bistrița Aurie alluvial sediments (left) and microscope image of a manganese oxide grains in thin section (right); Cracks can be observed both at the surface as well as internally.

The source of the manganese oxides in the alluvial sediments of the Bistrița Aurie River is most probably the syngenetic ferromanganese carbonate-silicate deposit, hosted by the black quartzites in the Tulgheș Metamorphic Unit, Ciocăneşti zone (Orata, Orata Mare, Colacu, Oița and Puiu) and Iacobeni zone (Nepomuceni, Arșița and Argestruț).

The oxidation zone comprises an impressive suite of manganese oxides, some of them being described for the first time in this area. The main mineral in this zone of oxidation is represented by psilomelane varieties: ebelmenite, lithiophorite, rankinite, lampadite and asbolane (Hîrtopanu, 2004; Munteanu et al., 2004, Ciortescu et al., 2014b).

The manganese oxides from Neagra Șarului River sediments occur in all samples, except those from upstream. From the total of heavy minerals, this group has a proportion ranging from 5.35 (± 0.75)% and 8.70 (± 0.95)%.

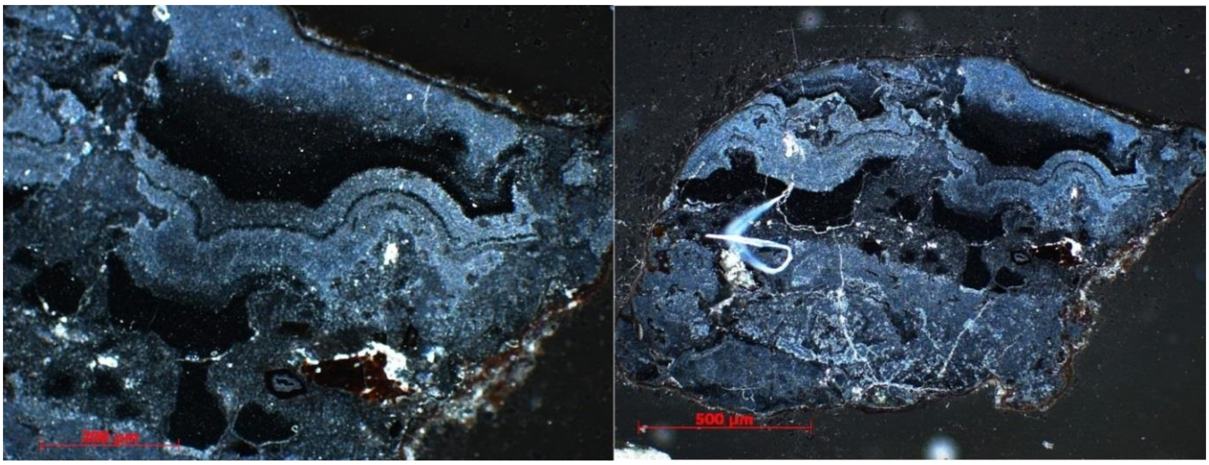


Fig. 18 Microscope images of a manganese oxides colomorfe depositions.

The source of the manganese oxides in the alluvial sediments of the Neagra Șarului River is most probably the syngenetic ferromanganese carbonate-silicate deposit, hosted by the black quartzites in the Tulgheș Metamorphic Unit, from Șarul Dornei - Dealul Rusului region (Ciortescu, 2014e). In thin sections the manganifere grains from alluvial sediments shows a typical growth pattern typically for secondary oxides with colomorph and colloidal deposition (Fig. 18). Such structure is often identified for aggregates as psilomelane, coronadite and manganifere cryptomelane from belonging to the deposits mentioned above (Hirtopanu, 2004).

X-ray diffraction patterns of the samples collected from alluvial sediments of the Bistrita Aurie and Dorna rivers indicates the presence of hausmannite and manganite.

## Chapter IX. STUDY OF THE CLINOPYROXENES FROM DORNA, NEAGRA ȘARULUI RIVER SEDIMENTS

Pyroxene is the most abundant heavy mineral in the alluvial sediments of the Dorna River, ranging from 19.46 (± 1.48) to 40.15 (± 0. 75) %. This group of minerals is entirely missing from the Bistrița Aurie alluvia. Transparent or translucent crystals have colours from dark green to yellow-green. The degree of roundness of the crystals varies from very angular to the angular. EDS spectra mostly indicate the presence of augite and, occasionally, enstatite.

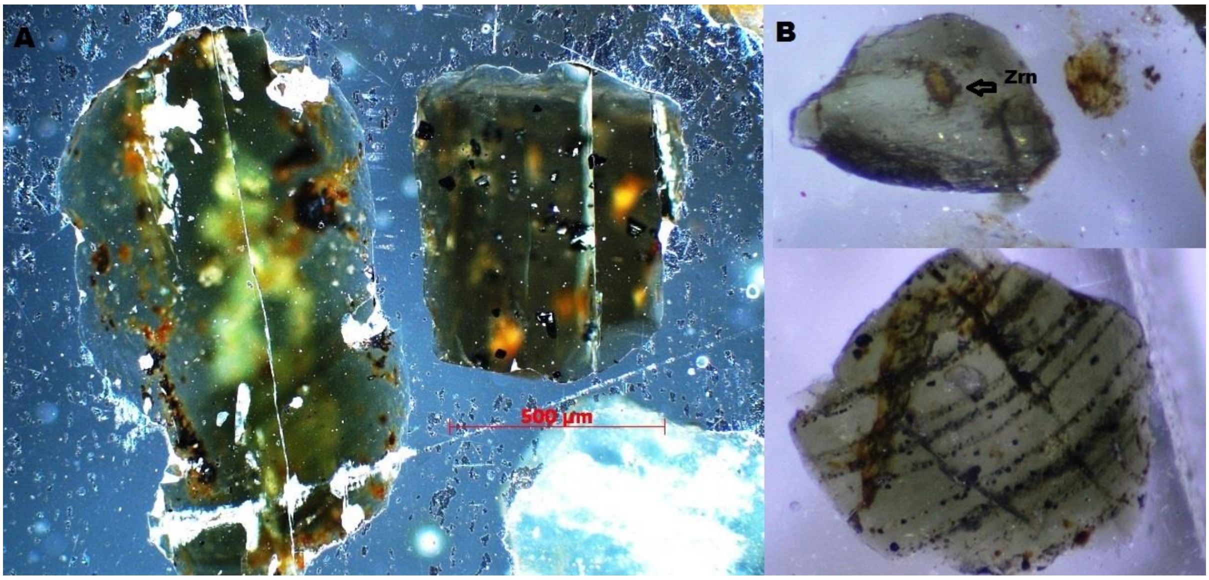


Fig. 19 A Microscope image of some pyroxene grains and their inclusions; B Image from binocular microscope of some pyroxene grains and their inclusions (Ciortescu et al., 2014e).

The major element compositions indicate the presence of augite and diopside ( Fig. 20 A). The enstatite presence alongside augite (Fig. 20 B) confirms the volcanic source of the clinopyroxene grains.The most likely sources of the pyroxenes from the alluvial concentrates are the pyroxene-andesites of the Călimani Volcanic Complex occupying most of the Dorna and Neagra Șarului river basins.

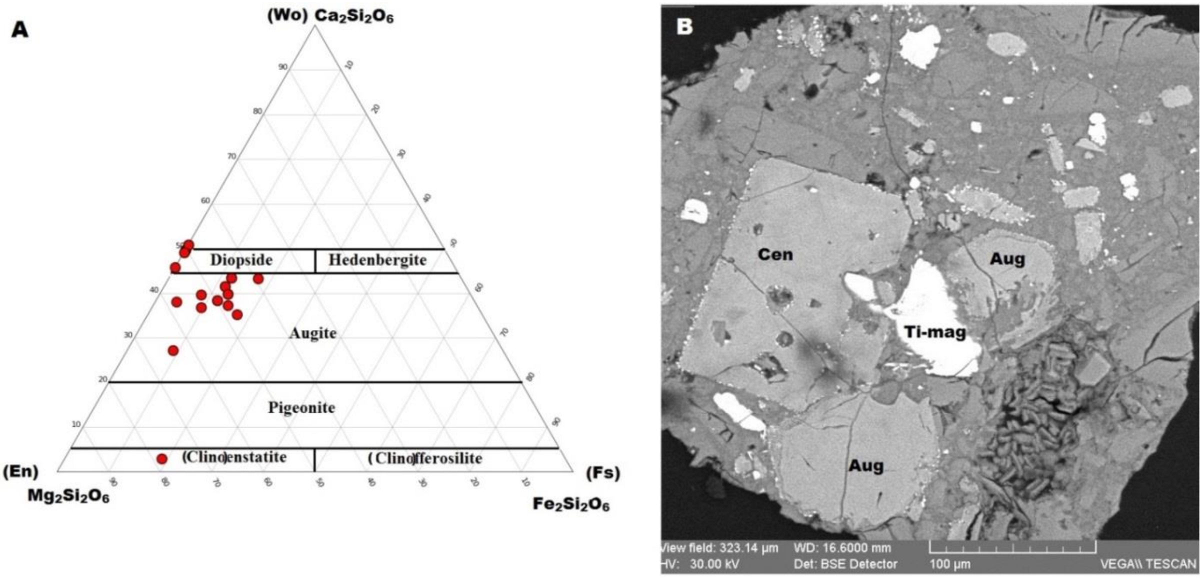


Fig. 20 A – The major oxide composition of the alluvial pyroxenes projected in to the Wo- En- Fs diagram (Ciortescu et al., 2014); B – BSE image (backscatter electron image) of an aggregate with enstatite, augite and Ti-magnetite.

Inclusions in pyroxene comprise a great number of phases (Fig. 19 A, B), such as ilmenite, titanium-magnetite, hematite, zircon, etc (Fig. 19 B) (Ciortescu et al., 2014e).

Also an opaque variety of pyroxene shows a strong ferromagnetism, which can be separated together with the magnetite grains. Most likely this is because numerous ferromagnetic inclusions (magnetite and Ti-magnetite) (Ciortescu et al., 2014).

X-ray diffraction patterns of the ferromagnetic fraction indicate the presence of wollastonite, while the diffractograms performed on alluvial concentrates highlight the presence of the diopside.

## Chapter X. OTHER HEAVY MINERALS FROM BISTRIȚA AURIE, DORNA AND NEAGRA ȘARULUI RIVER DEPOSITS

Among the heavy minerals described in alluvial sediments of the river Bistrița Aurie, Dorna and Neagra Șarului, in smaller or greater proportions, we can remember: pyrite, staurolite, apatite, chlorite, chloritoid, biotite, muscovite, molybdenite, pirotite, olivine, epidote, galena, hyperstene, monazite and zircon.

### X.1 Distribution of the pyrite from Bistrița Aurie, Dorna, Neagra Șarului river sediments

As magnetite and augite, pyrite was identified in all samples of sediments collected along the Neagra Șarului River, with maximum concentration at the bottom (downstream). This mineral varies widely from 3.82 (± 0.65) to 10.94 (± 1.03) % (Ciortescu et al. 2014e).

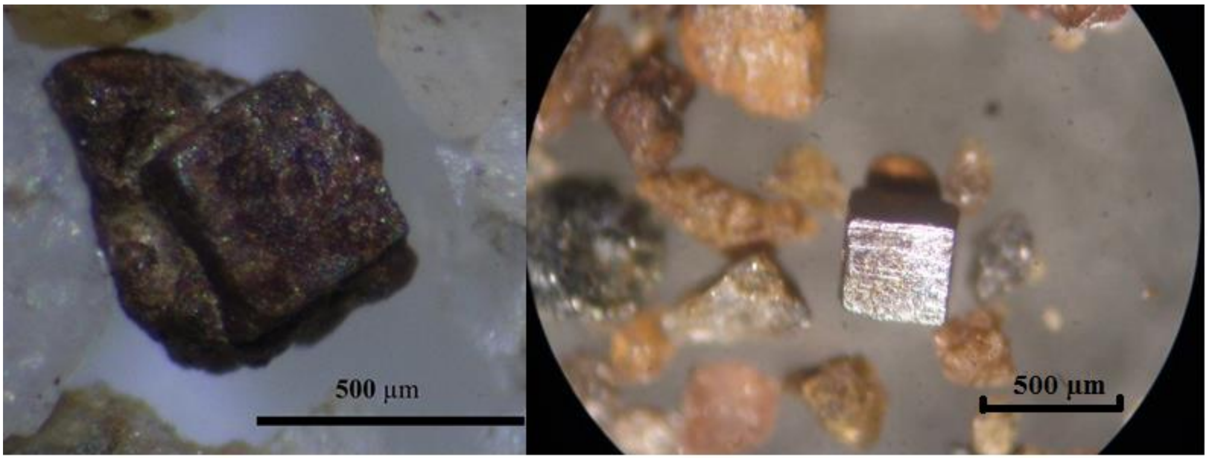


Fig. 21 Pyrite crystals from Dorna River alluvial deposits (Ciortescu et al. 2014b)

Pyrite occurs in two forms: the common form, cubes well developed (Fig. 21), and less frequent - composed of irregular aggregates. The dominant color is yellow and brassy, but many grains are tarnished. Hydrothermal assemblies of high to low temperature that characterize the contact zone of the intra-caldera monzodioritic intrusions from Călimani Mountains (Iancu and Kovaci, 2010) provides a continuous source of pyrite in rivers sediments. The presence of pyrite as inclusions in clynopyroxene crystals suggests also epigenetic origins of this mineral. Pyrite from Dorna river alluvial deposits has the same type and origin as that of Neagra Șarului river basin (Ciortescu et al. 2014e).

### X.2 Distribution of the apatite from Bistrița Aurie, Dorna, Neagra Șarului river sediments

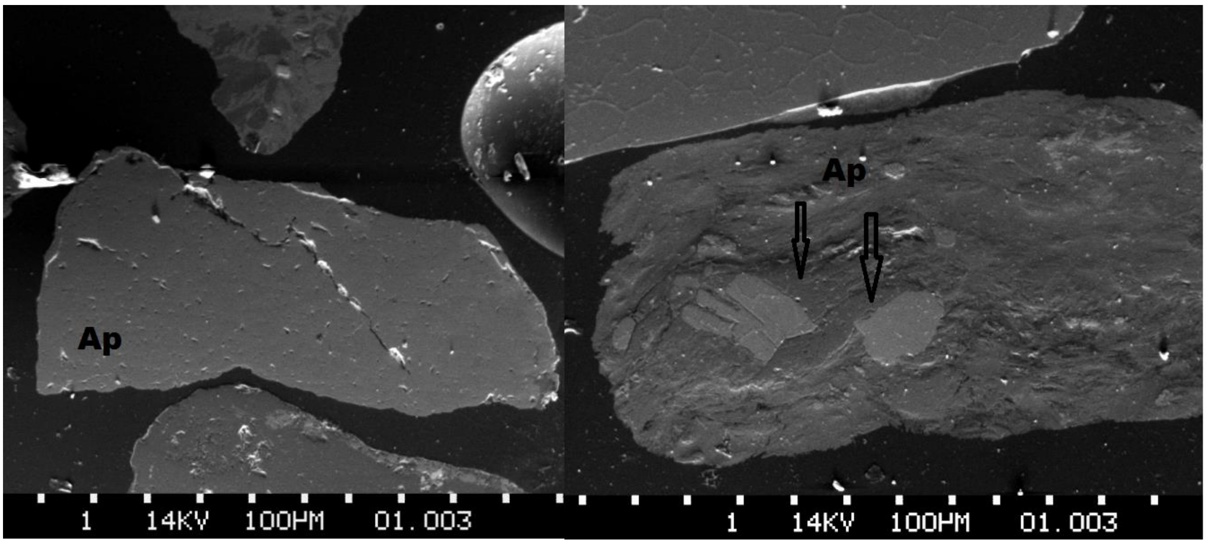


Fig. 22 BSE images (backscatter electron image) of some apatite grains (Ciortescu et al. 2014e)

Apatite from Neagra Șarului river sediments varies within wide limits, from 3.82 (± 0.65%) to 0.75% (± 0.29%). This mineral generally occurs either as single crystal (Fig. 22) or as aggregates of quartz and feldspar or as inclusion in other minerals (especially garnets).

Apatite grains show no inclusions or alterations. In Dorna and Bistrița Aurie river sediments it appears only as inclusion in garnets (Ciortescu et al. 2014b).

### X.3 Distribution of zircon and monazite from Bistrița Aurie, Dorna, Neagra Șarului river sediments

In the river sediments of the analyzed rivers, zircon and monazite appear only as inclusion in garnets (Fig. 23 A), iron and manganese oxides. Monazite was not described in any sample as a single crystal. Zircon occurs only in fractions of particle size less than 100 µm (Fig. 23 B), but there is an increased frequency of it as inclusion in various mineral grains, especially garnets and pyroxenes.

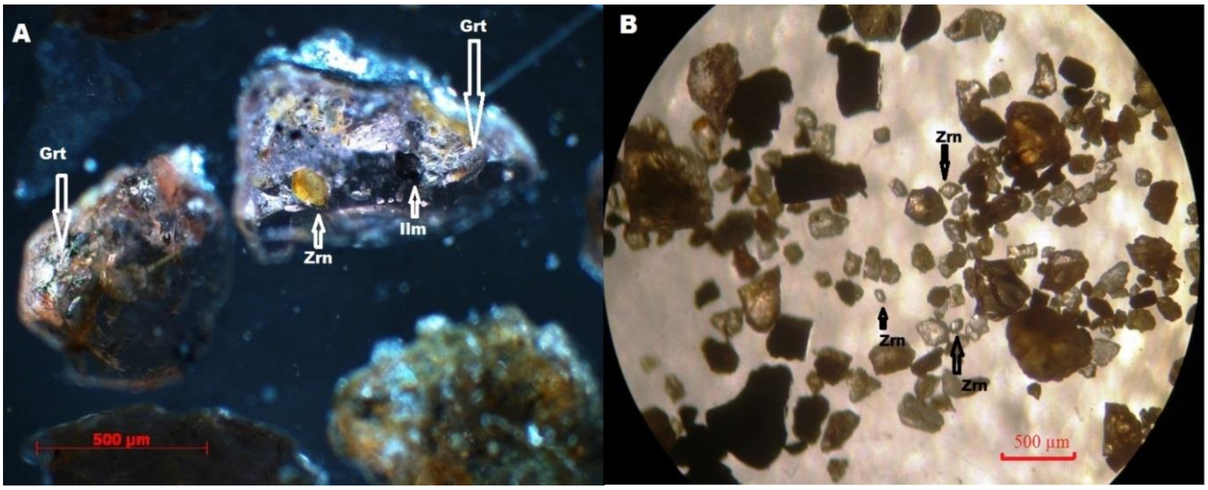


Fig. 23 A - Zircon and ilmenite inclusions in garnets, polarizing microscope image; B - Grains of zircon in the heavy fraction of alluvial sediments in the Ciocăneşti Town, binocular microscope image.

### X.4 Distribution of other heavy minerals from Bistrița Aurie, Dorna, Neagra Șarului river sediments

Among the heavy minerals with a low or random frequency in river sediments under discussion, we can remember: staurolite, chromite, olivine, epidote, molybdenite, galena, broggerite, etc. One interesting aspect is the presence of an aggregate derived from alluvial sediments of Neagra Şarului River containing chromite crystals (10 µm) along with epidote. Most likely, chromite comes from xenolite nodules commonly spread in the potassic andesites of the Călimani Complex (Seghedi et al., 2005). The staurolite was separated from alluvial sediments of the Bistrița Aurie River, in three different samples. Granules show a specific structure with inclusions of poikilitic quartz and ilmenite inclusions. Broggerite (U, Th) O2 was identified as inclusion in a garnet crystal.

## Chapter XI. IR SPECTROSCOPY STUDY OF HEAVY MINERALS FROM BISTRIȚA AURIE, DORNA, NEAGRA ȘARULUI RIVER SEDIMENTS

For IR analysis of heavy minerals from studied river basins have been used a istrument EQUINOX55, which belongs to Capodimonte Astronomical Observatory of Naples. The spectral region is NIR-IR, and spectral range lies between 428.1194 and 4971.5876 cm-1.

28 samples, were selected from grain size fractions between 2 and 0.125 mm. Six of analyzed grains from different samples were identified as garnet, with the dominant term almandine.

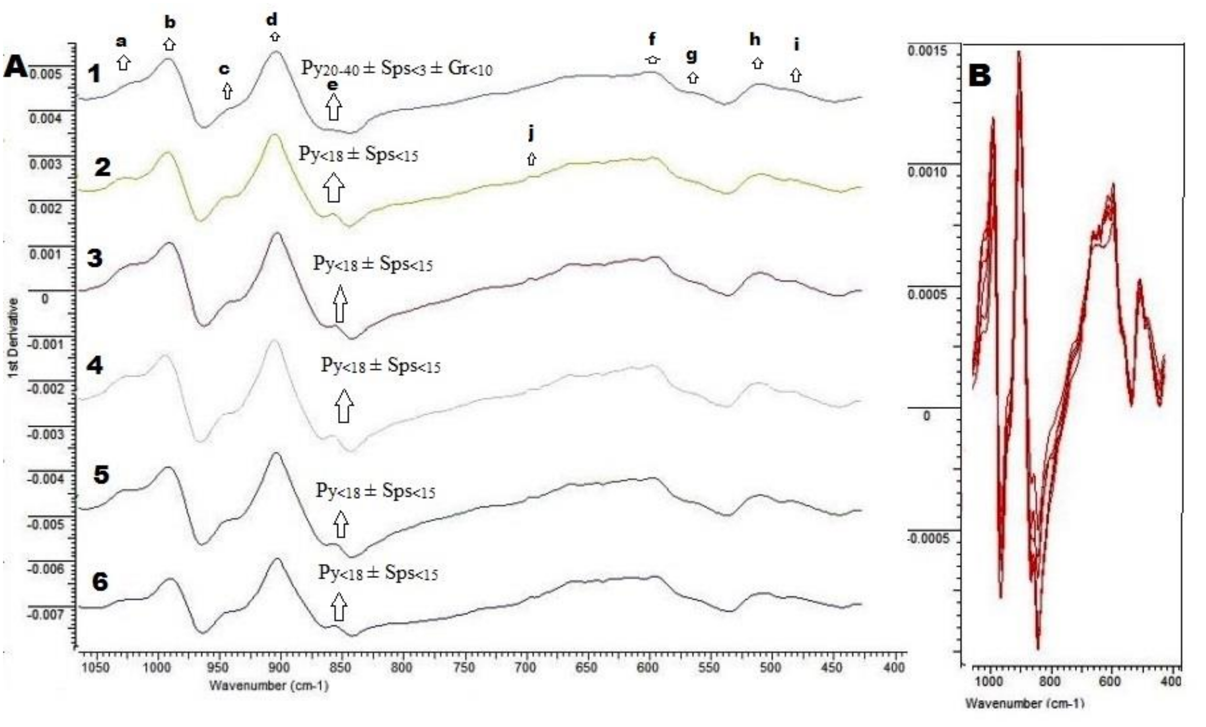


Fig. 24 A- IR spectra and representative spectral domains for garnet grains from Bistrița Aurie, Dorna and Neagra Șarului river basins; B- The overlapping degree of the alluvial garnet IR spectra.

No large deviations are shown for the analyzed garnet grains. They overlap presenting only small spectral deviations (24 B). The most obvious is the absence of the band from 865-864 cm-1 for the crystal 1. After Holmeister et al. (1996), the absence is due to pyrope content between 20 and 40%, ± spessartine and grossular (present in small amounts). For other spectra (2, 3, 4, 5, 6) of of the Fig. 24, this domain is highlighted. The more is pronounced, the almandine component is higher.

Also, in the first spectra could be observed the absence of the j band. Most likely it can be included in the group four of garnet classification while the rest of spectra can be assigned to groups one and two. So, the garnet No. 1 is collected from the locality Ciocăneşti, which reinforces the claim that the garnets with high pyrope content have their source in the upper basin of the Bistrița Aurie.

It was highlighted no major spectra difference depending of the garnet color and opacity of each analyzed crystal. Also, this method led to the identification of magnetite and pyroxene grains. Thus, from the total of analyzed grains, four of the minerals are identified as pyroxene, with the final term augite. Unlike IR spectra of garnet, those for pyroxene more have striking differences.

## CONCLUSIONS

This study provides additional information regarding the mineralogy and geochemistry of the heavy minerals from the alluvial sediments of the Bistrița, Neagra Șarului and Dorna rivers. Thus, for most minerals, the main source certain or possible areas were identified. There have also been remade the differences and similarities between the main studied areas and their determinants.

This paper is the only national study on heavy mineral geochemistry, subject for a doctoral thesis. The researches focused on the versatility and applicability of heavy minerals techniques. It was intended that, through physical and chemical properties of heavy minerals, to achieve an insight into the petrology nature of the sediment sources.

In the basins of the three studied rivers, following minerals are: garnet, clinopyroxene, manganese oxides, magnetite, titanomagnetite, maghemite, titanomaghemite, iron oxides, titanium oxides, ilmenite, chlorite, chloritoid, pyrite, apatite, zircon, monazite, epidote, hypersten, biotite, muscovite, etc.

Taking into account the chemical composition, the detrital garnet grains can be divided into four distinct groups having different sources. The most problematic group is represented by detrital garnet grains with a high content of pyrope (25-40% Py) and low in calcium. This type, which belongs to the fourth group, presents a chemical composition that indicates the source from high-grade metamorphic rocks, and the pyrope content reveals the granulitic character, being highlighted also by the IR spectroscopy. Therefore, the high content in pyrope is only an indication of a high-grade metamorphic event recorded in the metamorphic history of the Crystalline-Mesozoic Zone. Titanium mineral species identified in alluvial concentrates are: rutile, ilmenite, leucoxene, titanite and titanomagnetite. Approximately 40% of the analyzed titanium grains have an average concentration considered very close or identical to the ideal stoichiometric value of 52.6%. TiO2 concentration (> 50%) over 90% of titanium oxides analyzed in alluvial sediments is a key parameter in assessing the quality of a potential deposit. This increases the value of any economic potential. The source of the ilmenite can be attributed without any problems to medium grade metamorphic rocks of the Bretila and Rebra Metamorphic Units, while that of rutile is attributed to the Tulgheş Metamorphic Unit.

Most analyzed pyroxene crystals have augite subordinate diopside as final term. The presence of enstatite alongside augite confirms the volcanic source of pyroxene grains. Their source is represented by the andesites from Călimani Volcanic Complex, occupying most of the Dorna river hydrographic basin, especially Neagra Şarului. Some of the heavy minerals are also characterized by IR spectroscopy.

Among the heavy minerals identified in alluvial sediments there can also be mentioned: manganese oxides, iron oxides, manganese and iron oxides, staurolite, zircon, pyrite, galena, epidote, etc.

Therefore, this paper aims to study heavy minerals in the alluvial sediments of the river Bistrița Aurie, Dorna and Neagra Şarului, in order to characterize in detail the mineralogy and chemistry. The study also aims granulometric studies for establishing the sorting degree, transport mode and storage. Nevertheless, the ultimate purpose is the determination of an eventual economic potential, as well as emphasizing, wherever presumably, of the possible sources and their reconstruction.

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