# THE TRANSFER OF CERTAIN CONTAMINANTS BY MEANS OF SURFACE AND UNDERGROUND WATER-FLOWS IN THE CATCHMENT AREA OF ARIEŞ STREAM, ROMANIA

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*Abstract*. Within an area heavily concerned by mining activities, chemical analyses have been performed in order to estimate the quality of the surface water and of the groundwater, by assessing also the concentrations of Ba, Mn, Fe, Cu, Zn, Ni, Cr, Cd, Al, Pb, Sb, As adsorbed on the surface of the suspended particulate matter (SPM). The investigations have addressed a 108 km long section of Arieş stream. The analyzed nutrients, namely $NH_4$, $NO_2$ and $NO_3$, are liable to accumulate within the phreatic groundwater, the corresponding concentrations being higher in groundwater as compared to those in the surface water. In contrast to the nutrients behavior, there is noticed that concentrations of arsenic and of heavy metals in the surface water are larger than those in hyporheic water. Those contaminants are yet mainly conveyed by means of the SPM, which have the ability to attach and to concentrate large amounts of undesirable elements.

*Key words*: suspended particulate matter, heavy metals, nutrients, mining area, hyporheic zone, Arieş.

## 1. INTRODUCTION

The important part played by the *suspended particulate matter* (SPM) in the contaminants and nutrients transport by surface flows and by groundwater is currently widely accepted and intensively investigated (BOGATOV & BOGATOVA, 2009; CUSTER *et al.*, 2009). It is an established fact that most elements subject to high toxic potential are either partly, or entirely conveyed by means of the SPM (BOULT, 1996; DRYSDALE *et al*., 2001; POINT *et al*., 2007; HERBERT JR., 2006; TAYLOR, 2007; RIEUWERTS *et al.*, 2009).

In terms of experimental approach, there are two different ways for assessing the concentrations of heavy metals attached to SPM, namely a direct, and an indirect one. The direct assessment methods consist in separating the suspensions, as a general rule by means of filtering, after which the separated matter is digested and analyzed (HOROWITZ, 1986; FILIPEK *et al.*, 1987; NORDSTROM *et al.*, 1999; ÖDMAN *et al*., 1999, 2006; RUSE *et al*., 2000). The indirect assessment consists in separately analyzing the filtered and the unfiltered water sample, and in ascribing the difference in concentration between the two analyzes to the concentration of the element attached to the SPM (CIDU & FRAU, 2009; GAMMONS *et al.*, 2005; POKROVSKY & SCHOTT, 2002;

CORTECCI *et al.*, 2009; GUÉGUEN *et al.*, 2004). A comparative study of the results obtained through the two methods has been performed by BUTLER *et al.* (2008).

Within the Arieş stream catchment area, intense mining activities have been carried out since long time ago and are still being conducted nowadays, resulting in a highly detrimental impact on the quality of the surface water and of the groundwater. The mines, the quarries, the waste heaps, the tailing ponds, the fluid pipes and the ore processing facilities – all of them are major pollution sources, especially as far as the heavy metals are concerned (LUCA *et al.*, 2006). In this respect, a series of studies have already addressed the pollution of the surface water of that area (FORRAY & HALLBAUER, 2000; FLUVIO, 2006; FLOREA, 2007; SENILA *et al.*, 2007). The present study investigates the distribution of certain heavy metals, of arsenic and of the species of nitrogen, both in the surface water, and in the groundwater. There is also outlined the part played by the SPM in the transfer of the concerned contaminants, by using a direct assessment method.

## 2. THE STUDY AREA

The stream Arieş is the most important right-hand side tributary of Mureş river, stretching along a total length of 166 km between its head waters and the junction with the previously indicated main collector, while its catchment area extends over 3005 $km^2$ and its multi-annual average flow amounts to 25.6 $m^3/s$ (***, 2008). Starting from its headwaters, located in the southern part of Bihor Mountains, the stream-course of Arieş further separates the Mountains Metaliferi (located to the south), from the mountain-body Muntele Mare (located to the north), then it crosses the northern part of Trascău Mountains, to finally enter the wide depression of Turda. Starting from the village Gârda de Sus downstream, the valley consists of a gorge that nevertheless includes also a series of wider sections which correspond to a series of small basins having either a tectonic-structural, or an erosional origin, and which are positioned at the junction with the most significant tributaries (Gârda, Albac, Vadu Moţilor, Arieşul Mic, Sohodolu, Bistra, Ocoliş, Abrud, Şesii etc).

A wide variety of lithological units occur within the considered catchment area, including Paleozoic or Precambrian age metamorphic rocks, Jurassic age limestone deposits and ophiolites, Cretaceous age sandstones and limestone, as well as andesites that bear rich ore accumulations.

In the median, as well as in the upper catchment areas of Arieş stream (in the towns Roşia Montană, Câmpeni, Abrud, Baia de Arieş, etc), mining, as well as ore processing industries have a long-lasting tradition, being nowadays still well developed. To the mining works there are yet associated a multitude of tailing ponds which behave as permanent pollution sources for the surface and underground water flows (Fig. 1).

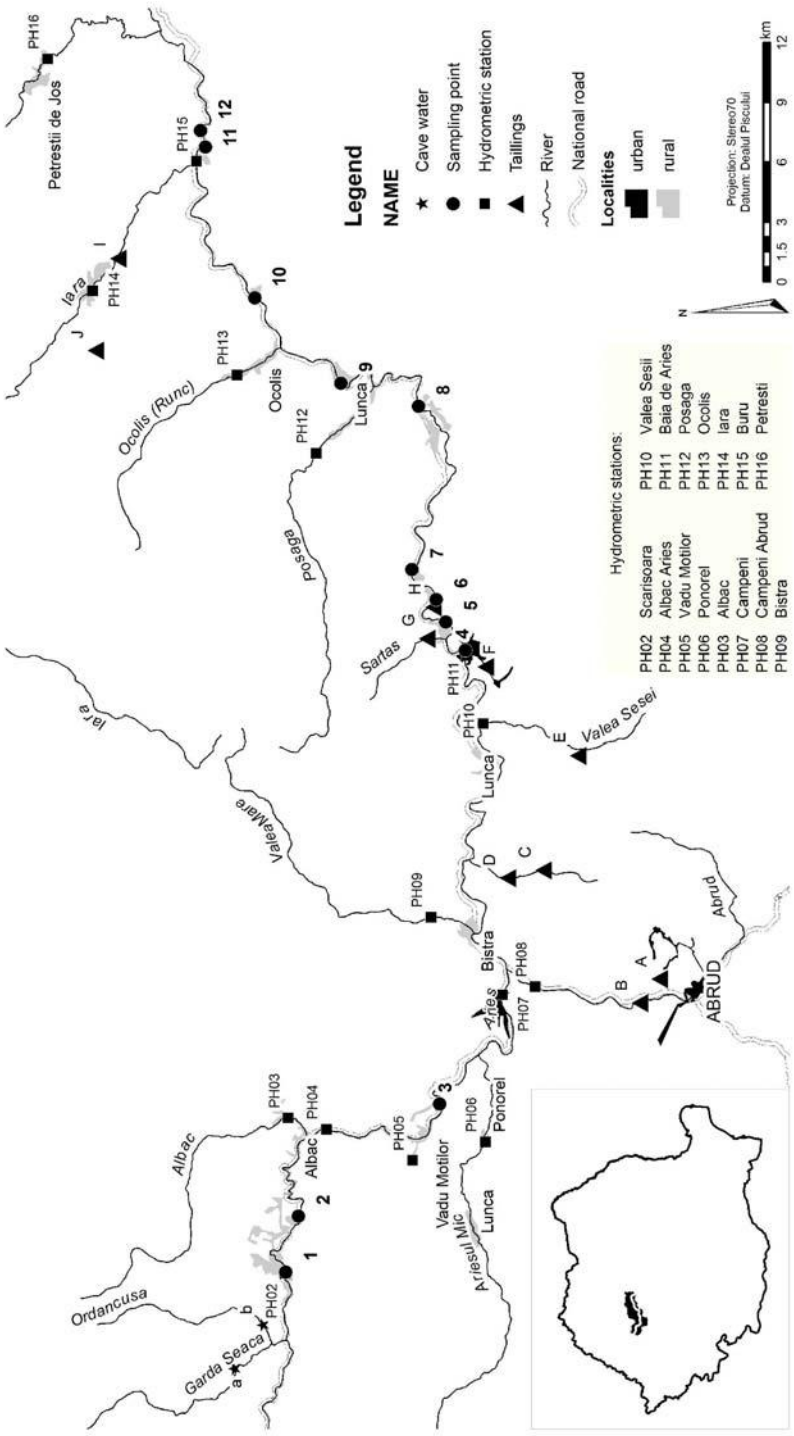


Fig. 1 – Location map indicating the surface and underground water sampling sites, the flow gauging stations and the main tailing ponds associated to the mining works located within the Arieș stream catchment area. The indicated tailing ponds are: **A** – Săliște, **B** – Gura Roșiei, **C** – Ștefanca 1, **D** – Ștefanca 2, **E** – Valea Șesei, **F** – Valea Cuții, **G** – Valea Sărtașului, **H** – Brăzești, **I** – Făgetu Ierii și **J** – Bărișoara. Cave water: a – Cotețul Dobreștilor, b – Peștera lui Ioanele cave.

## 3. MATERIALS AND METHODS

### 3.1. FIELD METHODS AND SAMPLE COLLECTION

Along the stream-course of Arieş, between the villages Scărişoara and Buru, a number of 12 common stations have been set up in order to collect samples of surface-water and of groundwater. All the water samples have been collected on 18 April 2008. The water-samples from Arieş stream have been collected directly in sampling bottles, at least 1 m away from the river-shore, in places where the thickness of the stream-water layer exceeded 20 cm. The groundwater samples have been collected according to the Bou-Rouch procedure (BOU & ROUCH, 1967; BOU, 1974).

In correspondence to the sampling sites, landform surveys have been carried out along lineaments positioned transversally with respect to the stream-course: specifically, two lineaments were surveyed on the right-side shore of the stream, while other ten lineaments were surveyed on its left-side shore. In selecting the positions of the lineaments and of the groundwater sampling holes, the following criteria have been taken into account:

- the position and the extent of the landform within the valley, as well as its relationships with landforms occurring at higher elevations;
- the physical features of the sedimentary deposit;
- the distance between the groundwater sampling hole and the actual stream-border;
- the groundwater sampling hole position with respect to the potential sources of pollution.

A number of seven groundwater sampling holes are located either quite close to the actual border of the stream, or within the lower floodplain of Arieş, being thus influenced by the variations of the stream water level, three other are located within the higher floodplain, two are positioned at the bottom of the lower terrace scarp, and one on the terrace tread (Table 1).

When collected, water samples were filtered *in situ* by means of a Chromatography Research Supplies filtering system, provided with a manual Nalgene vacuum pump. Pre-weighed (Kern 770–60) MF-Millipore Membrane, mixed cellulose esters of 0.45 μm porosity and of 47 mm diameter have been used for filtering. Each filtered membrane was washed in ultra-pure water before the experiment and used only once. During filtration, the first 250 mL of solution were discarded, thus allowing the saturation of the membrane surface prior collecting the filtrate. The filtered membranes with the collected material have been stored in individual polystyrene Petri dishes, both during their shipment and in laboratory, in refrigerating boxes at 4°C.

*Table 1*

Sampling stations set up along Arieş stream in order to the collect surface-water and groundwater samples

| Station | Distance between the surveyed lineaments (km) | Border of the stream | Distance to the stream border (m) | Landform |
|---|---|---|---|---|
| 1 – Scărişoara 1 | 0.00 | left | 7.80 | Bottom of the lower terrace scarp |
| 2 – Scărişoara 2 | 4.95 | left | 2.50 | Higher floodplain |
| 3 – Vadul Moţilor | 22.77 | left | 10.50 | Lower floodplain |
| 4 – Baia de Arieş | 60.20 | left | 3.50 | Higher floodplain |
| 5 – Sărtaş | 63.06 | left | 1.20 | Bottom of the lower terrace scarp |
| 6 – Brăzeşti 1 | 65.54 | left | 2.50 | Streambed |
| 7 – Brăzeşti 2 | 68.06 | right | 4.50 | Streambed |
| 8 – Sălciua de Jos | 79.92 | left | 6.15 | Streambed |
| 9 – Lunca Arieşului | 88.04 | left | 12.30 | Higher floodplain |
| 10 – Vidolm | 95.79 | right | 13.15 | Lower floodplain |
| 11 – Buru 1 | 107.50 | left | 5.00 | Lower floodplain |
| 12 – Buru 2 | 108.42 | left | 5.55 | Terrace tread |

The water temperature was measured on site by using a Crison portable thermometer TM65 with Immersion probe Pt 1000 sensor (measuring error ≤ 0.2°, reproductibility ±0.1°C). When samples were being collected, two Crison PH 25 portable instruments have been used in order to perform all pH measurements (5051 Electrode with integrated Temperature Probes ATC, NIST-traceable pH buffer solutions pH 4.01 and 7.00) and Eh measurements (52 62 Pt Electrode, 220 and 468 mV redox standard solutions), according to the recommendations of WILDE *et al.* (2006), and respectively of NORDSTROM & WILDE (2005).

### 3.2. ANALYTICAL METHODS

In laboratory, filtered membranes were dried at room temperature and then weighed to the nearest 0.01 mg to determine the mass of SPM in the known volume of filtered water. The filters were then digested at room temperature for 48 h with 5 ml of 1:1 solutions Ultrapur 60% $HNO_3$ and 30% HCl (Merck). This acid mixture was chosen to dissolve effectively the minerals more readily dissolved by weaker acids. The digest solutions were mixed occasionally during the digestion time. A 2.0 mL aliquot of the digest solution (not including any visible solid) was diluted to 50.0 mL with ultrapure water and analyzed by AAS. This process was repeated for duplicate unused filters and the average elemental content in the filter blanks was subtracted from the sample results. All the solutions were prepared with ultra-pure water (TKA Ultra Pure System GenPure, electric resistance 18.2 MΩ×cm).

The Na, K, Mg, Ca, Mn, Fe, Cu and Zn concentrations for the water samples and digested SPM were determined by means of standard flame-atomic absorption spectrometry methods. The Ba, Cr, Ni, Cd, Pb, As, Sb and As concentrations were analyzed by standard electrothermal-AAS methods. The determinations were carried out with a Perkin-Elmer atomic absorption spectrometer, model AAnalyst 700, with deuterium arc background correction, equipped with an HGA-800 graphite furnace, and an AS-800 autosampler. Pyrolytically coated tubes with and without integrated platforms were used. The calibration lines were traced using solutions prepared from standard solutions CertiPUR® (Merck). The methods accuracy, precision and sensitivity were been tested by using the reference matters provided by Perkin-Elmer groundwater and wastewater pollution control certified reference materials.

The total alkalinity has been assessed by electrometrical titration with a 0.05 M HCl solution by a Gran titration procedure (ROUNDS, 2006). In most cases, determinations were made within 24 hours of sampling. All the concentration assessments for silica (PAKALNS & FLYNN, 1967), sulfate (AMINOT, 1974), chloride (FLORENCE & FERRAR, 1971), ammonium and nitrite (MACKERETH *et al.*, 1978), and nitrate (APHA, 1985) have been conducted in laboratory, by means of a molecular absorption spectrometer in the visible and ultraviolet spectra, of the Perkin-Elmer Lambda 25 model.

The total dissolved solids (TDS) content was calculated as the sum of the total dissolved-ion concentrations, by additionally making the adjustment of bicarbonate to carbonate ions (HEM, 1985). The speciation calculations was performed by means of PHREEQC, version 2.15.0.2697 (February 2008) (PARKHURST & APPELO, 1999), with the Lawrence Livermore National Laboratory database. Surface-water and groundwater densities were calculated with the CLEGG & WHITFIELD (1991) relations for the inter-conversion of concentration scales, based on the measured temperatures.

## 4. RESULTS

The values of the physical and physical-chemical reference parameters, as well as the components concentrations assessed in the framework of the present study, both for the stream-water of Arieş, and for groundwater collected from the corresponding sampling sites, are indicated in ANEX 1. For comparison reasons, the table includes also the analytical results obtained for water samples collected during the same time-period from two karst springs which are typical for that area, being located upstream with respect to Scărişoara village, namely Coteţul Dobreştilor (within Gârda Seacă valley) and Peştere lui Ioanele (within Ordâncuşa valley).

When overall considered, the temperatures of Arieş stream-water are quite similar, yet slightly smaller, as compared to those of groundwater (on the average 7.6°, as compared to 7.7°C). One still has to take into account the circumstance that

the measurements have been performed during one single day, by starting in the morning at the extreme upstream location (Scărişoara), and ending in the evening at the extreme downstream one (Buru), while inherently, during the corresponding time-interval, the Arieş stream-water warmed up.

Along the stream section of Arieş that extends upstream Baia de Arieş, the total dissolved solids (TDS) content is different (82.7 mg/L on the average) from that of the stream section that extends further downstream (122.7 mg/L on the average). Along the two distinct stream-sections mentioned above, no uniform increase of the TDS values can be noticed; instead, from one sampling site to another, there occur significant fluctuations which are undoubtedly controlled by the inflows provided by the tributaries of Arieş stream (Fig. 2). As expected, groundwater exhibits for that parameter much larger values, the corresponding average amounting to more than de 150 mg/L. It is worth noticing that along the stream section that extends form Baia de Arieş downstream, not only are groundwater TDS values largely exceeding those of the Arieş stream-water, but they also differ significantly from one sampling site to another, the latter circumstance suggesting distinct recharge mechanisms for each specific sampling site.

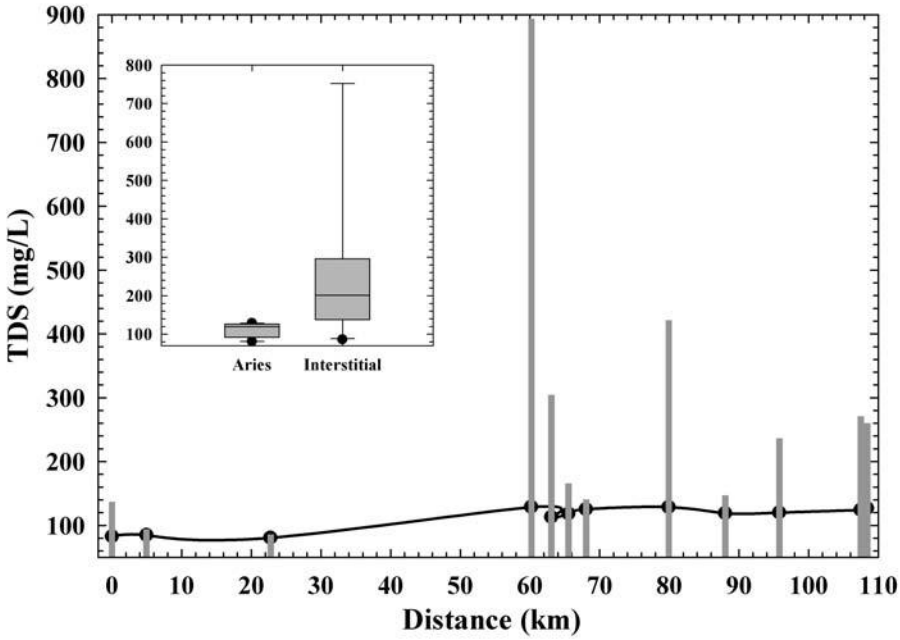


Fig. 2 – The total dissolved solids (TDS) content variation along the stream-course of Arieş (solid line) and at the corresponding groundwater sampling sites (bars). For all the diagrams of this type, the water flow direction has been chosen to be from left to the right, the kilometer 0 designating the extreme upstream sampling station (Scărişoara 1), while the kilometer 108.42 designates the extreme downstream one (Buru 2). The inset illustrates the TDS values global distribution for the stream Arieş, as compared to that of groundwater.

The distribution of the pH values is largely analogous to the variations of the TDS content. For the three sampling sites located along the Arieş stream section which extends from Baia de Arieş upstream, the stream-water pH is in excess of 8, while at the next three stations, from Baia de Arieş down to Brăzeşti 1, the pH values drop below 7 – a consequence of acid waste-water discharges due to the mining works. From the sampling station Brăzeşti 2 downstream, the Arieş stream-water pH values are steadily increasing, as a result of the bufer effect exerted by the prevalently carbonate substratum on which the river flows. The groundwater pH values exhibit an evolution which is analogous to that of the surface water, being yet worth mentioning that the groundwater average value is smaller (7.3) than that of the surface water (7.5). The redox potential difference values (Eh) behave similarly to the evolutions of the TDS contents and of the pH values. As normally expected, the Eh values for groundwater are smaller than those for the Arieş stream-water (by about 10 mV on the average). The recorded difference is not large, a circumstance which may be ascribed to the fact that the flow of Arieş stream was – as normally expected for the spring season – increased and it prevalently supplied the hyporheic zone.

The distribution of the $CO_2$ partial pressure values computed by means of the computer code PHREEQC is concordant with variations displayed by the TDS content and by the pH. Save for one sampling station (Lunca Arieşului), $P_{CO2}$ values for surface water are smaller than those computed for groundwater (Fig. 3). The latter exhibits the largest $P_{CO2}$ values in those stations where pH values also indicate an acid environment.

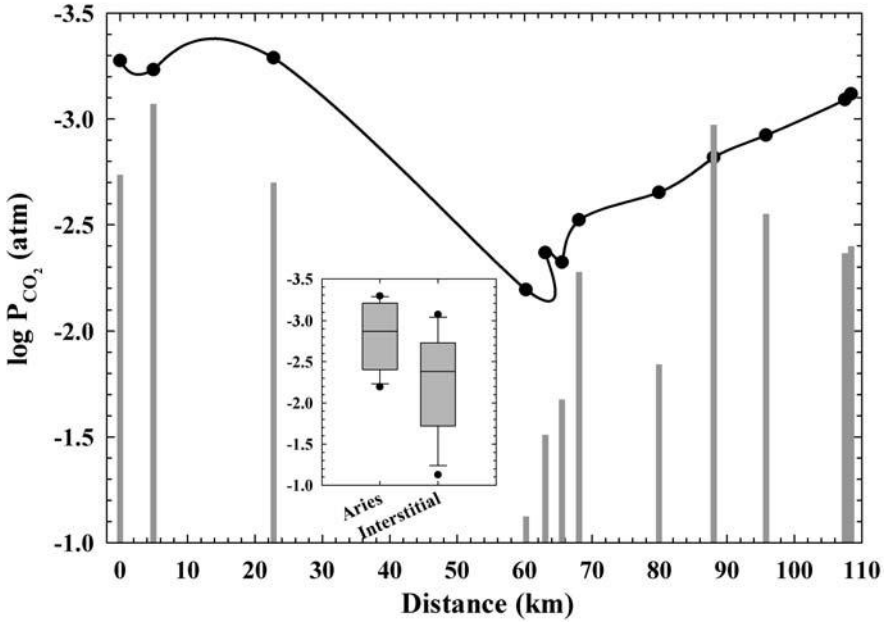


Fig. 3 – The $CO_2$ partial pressure variation along the stream-course of Arieş (solid line) and at the corresponding groundwater sampling stations (bars).

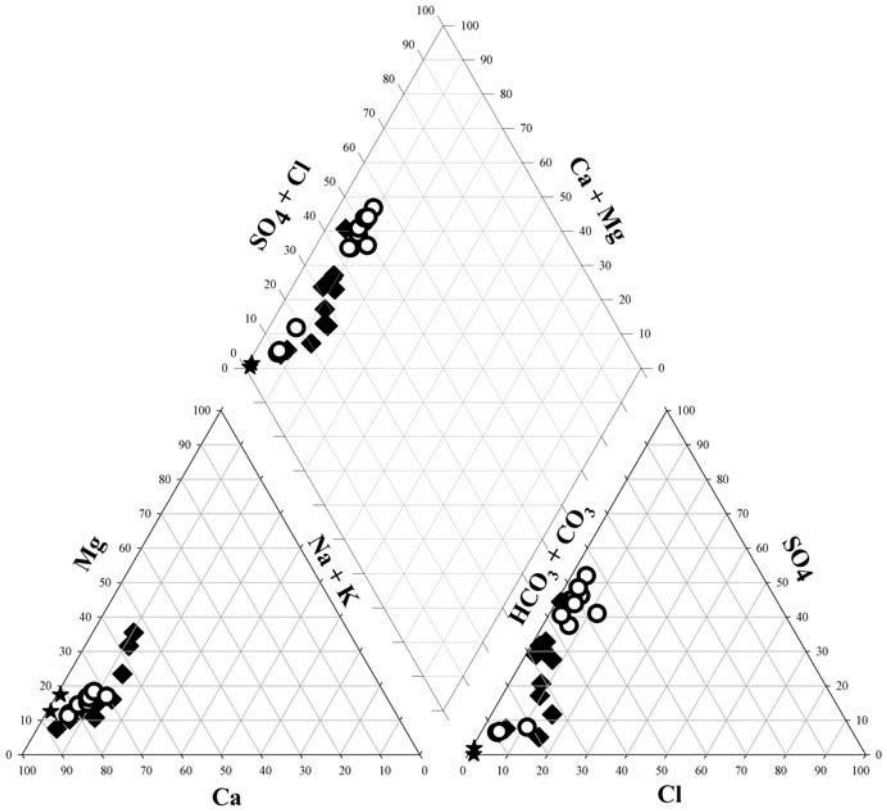


Fig. 4 – The hydrochemical facies, as indicated by the Piper diagram, for samples of surface water (circles) and of groundwater (diamonds) collected from the investigated area. The stars indicate the two investigated karst springs.

Generally speaking, samples of both surface water and groundwater collected from the Arieş stream catchment area belong to the $HCO_3$–Ca+Mg type. For water of both indicated origins, the prevalent cations, $Ca^{2+}$ and $Mg^{2+}$, taken together, amount to more than 40% of the ions total concentration. Within the Brăzeşti–Sălciua stream section (stations 8–10), the $Mg^{2+}$ percentage of the Arieş stream water increases to about 15%, which is largely in excess with respect to the average percentage of 6.5% recorded within the stream sections located further upstream and downstream, while the $Ca^{2+}$ percentage declines to 29.5%. This is in contrast to what was noticed in the case of groundwater, for which the $Mg^{2+}$ percentage was almost constant, namely about 7%. Alternatively, at the station Baia de Arieş and at all the stations located further downstream, the percentage of Fe in groundwater constantly amounted to 2%, while the percentage of Al ranged between 1 and 6%.

The average percentage of the prevalent anion, $HCO_3^-$, amounts to 35% for the surface water and to 29% for groundwater. It is worth noticing that for

groundwater samples collected from sites positioned downstream with respect to Baia de Arieş, the percentage of $SO_4^{2-}$ increases significantly to an almost constant value of 22%. That circumstance is, beyond doubt, due to the fact that the stream water of Arieş receives sulfate inflows, which are the final product of the oxidization of sulfide ores existing in the ore accumulations and in the waste heaps that occur within the catchment area, that final product eventually reaching the hyporheic zone.

Similarly to the previously discussed instances, distinct concentration distributions of ammonium ($NH_4$) and of nitrite ($NO_2$) are recorded in the two sections of the Arieş stream-course located upstream, and respectively downstream Baia de Arieş (Fig. 5).

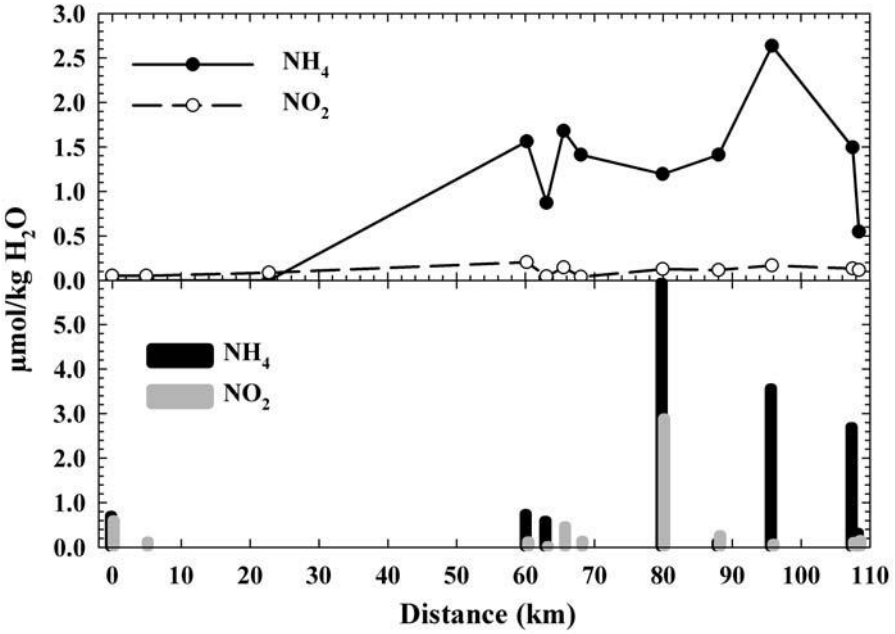


Fig. 5 – The variation of the molal concentrations of ammonium ($NH_4$) and nitrite ($NO_2$) along the stream course of Arieş (upper field of the diagram) and at the groundwater sampling sites (lower field of the diagram).

The upstream section is devoid of ammonium, while nitrite occurs only in small concentrations. In the stream section that extends downstream Baia de Arieş the corresponding concentrations become significant, as domestic waste disposal along the stream borders becomes increasingly frequent. The nitrate ($NO_3$) concentrations are relatively constant along the entire stream course of Arieş (Fig. 6), being nonetheless larger than those of the other two inorganic species of nitrogen.

Interstitial water is far richer in $NH_4$, $NO_2$ and $NO_3$, a circumstance which is due to the biogeochemical processes that operate there. Within that zone, especially at the aerobic/anaerobic interface, there is an interaction between the nitrification

and de-nitrification processes, both of them being controlled by the level of dissolved oxygen, of dissolved organic carbon (BRUNKE & GONSER, 1997; HINKLE *et al.*, 2001), and not in the last place, by the invertebrates fauna abundance (MARSHALL & HALL JR., 2004).

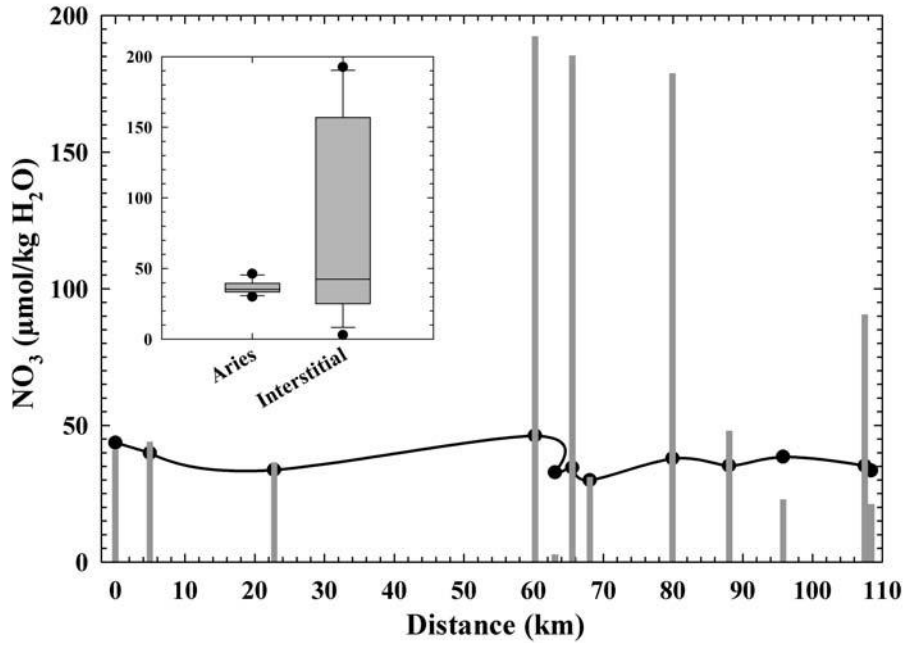


Fig. 6 – The variation of the molal concentrations of nitratate ($NO_3$) along the stream course of Arieş (the solid line) and at the groundwater sampling sites (bars).

The water samples collection moment has identified a certain level of concentration for arsenic and for heavy metals, all of which are derived, beyond doubt, from the mining works existing in the area crossed by the stream Arieş. The stream section located downstream with respect to Baia de Arieş is obviously more heavily contaminated, as compared to the stream section located further upstream. Specifically, no detectable concentrations of Cu, Zn, Cd and As could be identified along the indicated "upstream" section. Alternatively, the specified elements, as well as Fe, Mn, Cr and Al, are present along the entire stream course which extends downstream Baia de Arieş. Except for chromium, the concentrations of all heavy metals are much lower in the phreatic groundwater, as compared to the corresponding concentrations found in the stream water of Arieş, a circumstance which shall be given a detailed discussion below. There was also attempted an assessment of the Ni, Pb and Sb contents, yet in every instance the concerned concentrations were, both in the surface water and in the groundwater, below the detection limits of the specific analysis methods.

## 5. DISCUSSIONS

### 5.1. WATER EXCHANGES BETWEEN THE STREAM-COURSE OF ARIEŞ AND THE PHREATIC GROUNDWATER BODY

A first issue requiring to be discussed is the way in which reciprocal flow relationships develop between the stream course of Arieş and the phreatic aquifer. The diagram in Fig. 7 illustrates one of the landforms lineaments surveyed transversally to the stream course of Arieş. The lithological composition and the granulometry of the deposits crossed by the interstitial water sampling device are quite diverse. There have been identified fine sands, muddy sands, sandy mudstones, gravel and boulders, yet their distribution along vertical could not be specified along the entire length of the lineament. Only the surface layer could be realistically described.

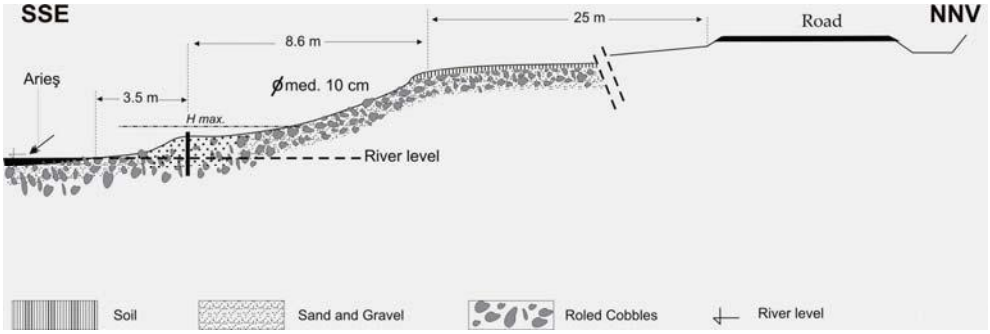


Fig. 7 – Landforms survey at the sampling station Baia de Arieş, along a lineament positioned transversally with respect to the stream course of Arieş.

Reciprocal recharge relationships exist between the streams network and the groundwater accumulations. The strength and the direction of the water exchanges are controlled (among other) by the aquifer formations permeability and by the recharge sources of superficial or underground origin. The water exchange between the stream Arieş and the phreatic accumulations located within the unconsolidated detritic deposits of the floodplain is controlled by the stream water-level. As a general rule, during drought periods, the streambed of Arieş is supplied by groundwater inflows provided by the deposits that build up the floodplain and the terraces. High discharge occurring during spring time, as well as summer time flash floods may induce temporary reversals in the groundwater flow direction, so that phreatic groundwater accumulations within the floodplain start being recharged by the stream water. This is the setting which favors the pollutants transfer from the stream course to the phreatic groundwater accumulations, the concerned process reaching its maximum intensity when the lower floodplain is actually flooded.

## 5.2. THE CONTAMINANTS TRANSFER BETWEEN THE SOLUBLE AND THE SPM DOMAINS

As the obtained analytical data indicate (Table 2), the stream water of Arieş contains significant concentrations of iron, manganese, and especially aluminum. Those elements are derived from the mining activities that are carried out in that area (LUCA *et al*., 2006). Specifically, FLOREA (2007) has identified excessively high concentrations of Fe, Mn and Al in the stream Abrud and in all its tributaries, being of common knowledge the fact that the entire catchment area of that stream is heavily affected and disrupted by the giant quarry which exploits the Roşia Poieni copper ore. The indicated exploitation facilities include three waste heaps, which extend over an area totaling more than 1 $km^2$. Those waste heaps are concerned by natural phenomena of erosion at the surface and in depth, which result not only in a contamination of water with heavy metals, but also in water becoming intensely acid, while significant inflows of suspensions also occur. Those suspensions accumulate mostly in the Valea Şesei tailings pond, which poses serious ecological threats to that area.

The Fe, Mn and Al contents of groundwater saturating the phreatic aquifer associated to Arieş stream are about one order of magnitude smaller than the corresponding contents of the surface water (Fig. 8). The weaker contamination of the

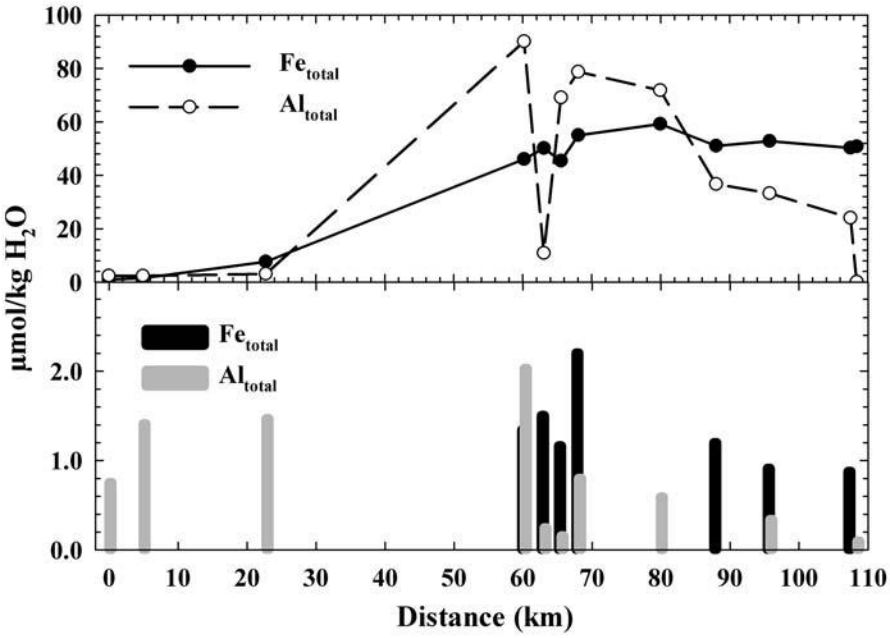


Fig. 8 –The variation of the molal concentrations of Fe and Al along the stream course of Arieş (upper field of the diagram) and at the groundwater sampling sites (lower field of the diagram).

hyporheic domain with those elements is due to the circumstance that in solution, they are liable to precipitate as hydroxides, generating fine colloids (GANDY *et al*., 2007; HARVEY & FULLER, 1998). The latter, although being precipitation products, behave in terms of transport mechanisms similarly to the dissolved compounds. The generation of colloids, prevalently as a result of the trivalent cations hydrolysis, has also a significant operational outcome. Colloids penetrate the 0.45 μm filtering membrane (KENNEDY *et al.*, 1974; BOULT, 1996). When water samples filtered in that way are analyzed by means of spectrometric methods (AAS or ICP), both phases – solution and colloidal – will be analyzed together, resulting in a positive deviation of the charges balance.

All the investigators having performed chemical-analytical studies in that area have reported that the stream water of Arieş included significant concentrations of Cu, Zn, Cd, As (FORRAY & HALLBAUER, 2000; FLUVIO, 2006; SENILA *et al*., 2007), comparable to the corresponding concentration values indicated by the present investigation. The main contamination source is Valea Şesei tailings pond. Copper is liable to be adsorbed on the Fe and Al colloids (GANDY *et al*., 2007), a circumstance which results, under normal conditions, in diminished concentrations. For instance, it is in very few samples collected from the stream water of Arieş, that SENILA *et al*. (2007) managed to detect, by performing ICP-AES analyses, concentrations of Cu exceeding the detection limit of the employed method (0.011 mg/L). Zinc is more mobile, a property that is proven by associated concentrations, which both the present study, and the above-indicated previous investigators, have shown to be larger than those of copper.

The most important characteristic outlined by our investigations is that arsenic and heavy metals concentrate on the SPM surface (Fig. 9). It becomes thus obvious that suspensions are the main agent in the contaminants transport.

The nature of suspended particles occurring in groundwater is highly diverse. Specifically, they may be solid fragments removed from the substratum by the flowing water, or particles generated within the very water body as a result of the latter becoming super-saturated with respect to certain components (e.g. metal oxyhydroxides), but they may be also living or decaying organisms, as well as their exudates. The active surface of those particles is the most important carrying-phase for heavy metals, being able to outpace significantly the transport by solution (MOREL, 1983; MUNK *et al*., 2002). As clearly noticeable in the diagram of Fig. 9, elements like Ni, Pb and Sb concentrate on the SPM surface, and as such their concentrations can be easily assessed, which is in contrast to the analysis of their soluble phase, which was not able to identify those elements in concentrations exceeding the detection limit of the employed methods.

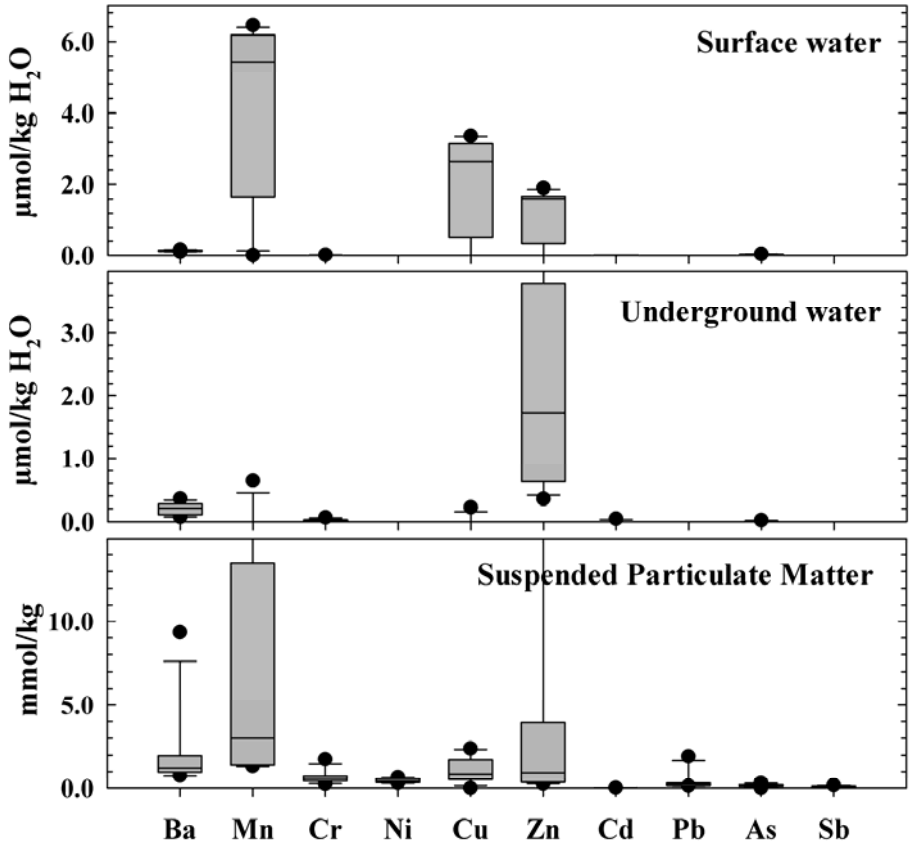


Fig. 9 – The concentrations distribution of certain heavy metals and of arsenic in the stream water of Arieş, in the interstitial water and adsorbed on the SPM surface.

## 6. CONCLUSIONS

By collecting surface water and groundwater samples from 12 collecting sites positioned between the villages Scărişoara and Buru, which were located 108 km one from another, on the Arieş stream valley, there have been outlined certain characteristics of the contaminants transfer that occurred in the indicated catchment area.

In this respect, the stream section which extends upstream with respect to Baia de Arieş, more specifically upstream the junction between Arieş and Valea Şesei, seems to be less affected by the mining activities carried out in that area. The analyzed nutrients, namely $NH_4$, $NO_2$ and $NO_3$, are liable to accumulate in the phreatic groundwater, their concentrations in the groundwater being more elevated than those in the surface water. Different from the nutrients, arsenic and a series of

heavy metals (Al, Fe, Cu, Zn, Cd) occur in surface water in higher concentrations, as compared to concentrations recorded in the hyporheic domain.

A multitude of complex chemical and biochemical processes contribute to attaching arsenic and heavy metals to the active surfaces of the suspended particles that occur in groundwater, to finally result in a concentration of those contaminants. The concentrations of certain elements, such as Ni, Pb, Sb, could be assessed for the phase which was adsorbed on the SPM surface, but not for the phase dissolved in the surface water or in the groundwater. That is why in an area heavily concerned by anthropogenic activities, suspensions have to be deemed as the main transfer agent for contaminants.

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*Annex 1*

Results of the chemical-analytical measurements performed for the surface-water samples collected from the sampling stations set up along the stream-course of Arieş, as well as for the corresponding groundwater samples (on 18 April 2008)

| No. | Station | water type | t | pH | Eh | TDS | $NH_4$ | Na | K | Mg | Ca | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | °C | | mV | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| 1 | 1-Scarisoara 1 | surface | 5.3 | 8.05 | 222.7 | 82.6 | 0 | 1.8 | 0.4 | 2.1 | 24.5 | 0.05 |
| 2 | 1-Scarisoara 1 | underground | 6.7 | 7.70 | 160.4 | 137.2 | 0.013 | 6.2 | 2.1 | 3.3 | 38.3 | 0 |
| 3 | 2-Scarisoara 2 | surface | 5.4 | 8.02 | 140.2 | 84.9 | 0 | 1.8 | 0.5 | 2.1 | 25.3 | 0.08 |
| 4 | 2-Scarisoara 2 | underground | 7.1 | 7.92 | 136.9 | 94.4 | 0 | 2.3 | 0.7 | 2.1 | 28.5 | 0 |
| 5 | 3-Vadul Motilor | surface | 5.8 | 8.01 | 154.1 | 80.5 | 0 | 1.9 | 0.6 | 2.5 | 22.1 | 0.43 |
| 6 | 3-Vadul Motilor | underground | 6.9 | 7.50 | 166.6 | 86.0 | 0 | 2.3 | 0.8 | 2.8 | 23.8 | 0 |
| 7 | 4-Baia de Aries | surface | 7.1 | 6.85 | 154.7 | 128.7 | 0.028 | 3.0 | 1.1 | 3.2 | 26.9 | 2.57 |
| 8 | 4-Baia de Aries | underground | 8.7 | 6.67 | 159.8 | 893.6 | 0.014 | 14.6 | 4.9 | 14.3 | 271.0 | 0.08 |
| 9 | 5-Sartas | surface | 7.3 | 6.92 | 151.7 | 113.0 | 0.016 | 2.7 | 1.1 | 3.4 | 24.2 | 2.80 |
| 10 | 5-Sartas | underground | 7.7 | 6.79 | 140.9 | 304.6 | 0.011 | 15.0 | 5.1 | 10.6 | 75.1 | 0.08 |
| 11 | 6-Brazesti 1 | surface | 7.4 | 6.92 | 146.5 | 118.4 | 0.030 | 2.6 | 1.2 | 3.4 | 24.1 | 2.54 |
| 12 | 6-Brazesti 1 | underground | 7.9 | 6.59 | 155.9 | 166.0 | 0 | 3.6 | 5.5 | 10.4 | 31.0 | 0.07 |
| 13 | 7-Brazesti 2 | surface | 8.0 | 7.10 | 171.5 | 125.3 | 0.025 | 2.8 | 1.1 | 3.7 | 25.1 | 3.07 |
| 14 | 7-Brazesti 2 | underground | 6.4 | 7.15 | 149.8 | 140.8 | 0 | 4.5 | 1.8 | 10.1 | 25.4 | 0.12 |
| 15 | 8-Salciua | surface | 8.4 | 7.27 | 170.5 | 128.7 | 0.022 | 2.8 | 1.1 | 3.6 | 27.3 | 3.31 |
| 16 | 8-Salciua | underground | 9.6 | 7.25 | 161.8 | 421.8 | 0.107 | 23.0 | 2.2 | 22.4 | 98.9 | 0 |
| 17 | 9-Lunca Ariesului | surface | 8.7 | 7.40 | 168.1 | 119.0 | 0.025 | 2.6 | 1.1 | 3.5 | 26.2 | 2.85 |
| 18 | 9-Lunca Ariesului | underground | 7.5 | 7.88 | 154.6 | 147.3 | 0.002 | 3.4 | 1.6 | 4.2 | 38.8 | 0.07 |
| 19 | 10-Vidolm | surface | 9.1 | 7.60 | 169.0 | 120.0 | 0.048 | 2.8 | 1.1 | 3.5 | 26.2 | 2.95 |
| 20 | 10-Vidolm | underground | 6.7 | 7.63 | 156.1 | 236.7 | 0.064 | 6.0 | 3.5 | 6.4 | 63.3 | 0.05 |
| 21 | 11-Buru 1 | surface | 9.6 | 7.71 | 165.1 | 124.2 | 0.027 | 3.0 | 1.3 | 4.1 | 26.6 | 2.81 |
| 22 | 11-Buru 1 | underground | 9.3 | 7.57 | 163.3 | 271.1 | 0.049 | 10.2 | 4.5 | 8.8 | 72.0 | 0.05 |
| 23 | 12-Buru 2 | surface | 9.5 | 7.80 | 168.2 | 126.7 | 0.010 | 3.0 | 4.5 | 4.0 | 27.2 | 2.83 |
| 24 | 12-Buru 2 | underground | 8.1 | 7.54 | 161.0 | 260.7 | 0.006 | 7.8 | 2.7 | 8.1 | 72.6 | 0 |
| 25 | Cotetul Dobrestilor | cave water | 6.5 | 7.56 | – | 174.5 | 0.003 | 0.5 | 0.5 | 7.4 | 57.4 | 0 |
| 26 | Pesterea lui Ioanele | cave water | 7.2 | 7.74 | – | 203.3 | 0.005 | 0.5 | 0.6 | 6.1 | 69.1 | 0.09 |

*Annex 1* (continued)

| No. | Mn | Cu | Zn | Ba | Cr | Cd | Al | As | $HCO_3$ | Si | $NO_2$ | $NO_3$ | $SO_4$ | Cl |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | mg/L | mg/L | mg/L | µg/L | µg/L | µg/L | µg/L | µg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| 1 | 0 | 0 | 0 | 18.5 | 0.233 | 0 | 65.2 | 0 | 78.3 | 2.5 | 0.002 | 2.70 | 4.5 | 2.1 |
| 2 | 0 | 0 | 0.02 | 26.9 | 2.057 | 4.650 | 20.4 | 0 | 118.7 | 2.8 | 0.028 | 2.54 | 6.0 | 13.3 |
| 3 | 0.02 | 0 | 0 | 14.0 | 0 | 0 | 62.8 | 0 | 80.4 | 2.4 | 0.002 | 2.47 | 4.8 | 2.5 |
| 4 | 0 | 0 | 0.04 | 14.9 | 0.184 | 0 | 38.1 | 0 | 90.1 | 2.3 | 0.006 | 2.73 | 5.1 | 2.8 |
| 5 | 0.03 | 0 | 0 | 15.6 | 0.180 | 0 | 83.6 | 0 | 69.0 | 2.6 | 0.004 | 2.08 | 5.3 | 5.5 |
| 6 | 0 | 0 | 0.05 | 11.0 | 0 | 0 | 39.5 | 0 | 80.0 | 2.5 | 0 | 2.26 | 5.5 | 3.2 |
| 7 | 0.34 | 0.21 | 0.11 | 13.4 | 0 | 0.498 | 2430.0 | 0 | 72.3 | 2.9 | 0.009 | 2.86 | 38.3 | 5.1 |
| 8 | 0.04 | 0.01 | 0.42 | 37.6 | 3.322 | 1.145 | 54.8 | 0 | 489.1 | 4.5 | 0.006 | 11.92 | 315.2 | 6.7 |
| 9 | 0.30 | 0.21 | 0.12 | 14.8 | 0.564 | 0.486 | 293.1 | 0 | 47.6 | 2.5 | 0.002 | 2.03 | 44.1 | 2.4 |
| 10 | 0 | 0 | 0.32 | 32.1 | 2.924 | 0 | 6.6 | 0 | 249.3 | 5.3 | 0.002 | 0.17 | 31.6 | 30.6 |
| 11 | 0.28 | 0.20 | 0.11 | 15.2 | 0 | 0.480 | 1863.0 | 0.78 | 61.2 | 2.5 | 0.007 | 2.14 | 41.6 | 2.3 |
| 12 | 0 | 0 | 0.25 | 30.7 | 7.221 | 0 | 4.2 | 0 | 103.5 | 5.0 | 0.022 | 11.49 | 37.8 | 3.4 |
| 13 | 0.33 | 0.20 | 0.11 | 12.1 | 0 | 0.468 | 2123.0 | 1.52 | 60.5 | 2.5 | 0.002 | 1.85 | 45.3 | 3.9 |
| 14 | 0 | 0 | 0.09 | 9.4 | 0 | 0 | 21.6 | 0 | 96.5 | 4.8 | 0.007 | 1.93 | 36.4 | 2.0 |
| 15 | 0.33 | 0.20 | 0.09 | 13.6 | 0 | 0.459 | 1936.0 | 1.40 | 64.2 | 2.7 | 0.006 | 2.34 | 44.9 | 2.9 |
| 16 | 0 | 0 | 0.25 | 48.5 | 5.017 | 0 | 15.9 | 0 | 333.1 | 4.9 | 0.133 | 11.08 | 61.4 | 25.3 |
| 17 | 0.34 | 0.18 | 0.11 | 16.8 | 0.451 | 0.482 | 990.0 | 1.57 | 54.8 | 2.6 | 0.005 | 2.18 | 43.6 | 2.4 |
| 18 | 0 | 0 | 0.04 | 14.1 | 1.968 | 0 | 0 | 1.02 | 103.7 | 3.5 | 0.013 | 2.98 | 34.6 | 2.3 |
| 19 | 0.35 | 0.16 | 0.11 | 18.5 | 0 | 0.392 | 896.0 | 2.25 | 66.5 | 2.9 | 0.008 | 2.38 | 37.8 | 2.3 |
| 20 | 0 | 0 | 0.10 | 24.3 | 2.043 | 0 | 9.1 | 1.50 | 158.5 | 3.6 | 0.004 | 1.42 | 64.0 | 4.6 |
| 21 | 0.28 | 0.13 | 0.09 | 21.2 | 0 | 0.297 | 649.0 | 1.88 | 57.8 | 2.7 | 0.006 | 2.18 | 39.7 | 8.6 |
| 22 | 0 | 0 | 0.13 | 38.3 | 2.450 | 0 | 0 | 0.73 | 205.0 | 3.1 | 0.006 | 5.62 | 46.9 | 13.7 |
| 23 | 0.30 | 0.13 | 0.10 | 19.4 | 0.230 | 0.295 | 2.4 | 2.04 | 62.4 | 2.7 | 0.005 | 2.07 | 42.0 | 3.5 |
| 24 | 0 | 0 | 0.15 | 39.7 | 0 | 0 | 2.6 | 0.88 | 179.9 | 2.6 | 0.008 | 1.32 | 60.2 | 12.1 |
| 25 | 0 | 0 | 0 | 4.6 | 0 | 0 | 59.4 | 0 | 202.2 | 1.1 | 0.006 | 3.05 | 0.3 | 1.7 |
| 26 | 0 | 0 | 0 | 6.9 | 0 | 0 | 43.6 | 0 | 232.4 | 1.2 | 0.005 | 3.58 | 3.6 | 1.0 |

# MINERALOGICAL ANALYSES IN VARIOUS CAVES FROM THE BĂILE HERCULANE AREA, THE CERNA PASSAGE

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*Abstract.* In this paper we present the results from the mineralogical analyses performed on samples from three caves in the Băile Herculane area. All minerals are recorded for the first time in the investigated caves.

*Key words:* endokarst, spelean mineralogy.

The Băile Herculane caves from where samples were drawn in order to perform mineralogical analyses through X-ray diffractometry are Peştera lui Adam, Gaura Ungurului Cave and the Grota Haiducilor Cave, (Fig. 1).

## 1. PEŞTERA LUI ADAM

This cavity, lays at the base of the first morphological level of the Malm-Neocomian limestone, developed in the mount of the Ciorici Peak, on the right slope of the Cerna Passage (under the Elisabeta Peak) which is lined with the Roman Hotel from the Băile Herculane balneal spa.

What makes this natural hole, consisting of two relatively parallel spaces (the Guano Gallery and the Aburi (Steam) Gallery summing to 169 m in length), so particular is the fact that, being a thermal cavity [with temperatures up to 36–38°C in the Guano Gallery and more than 45°C in the Aburi (Steam) Gallery] provides – during the hot season – an excellent shelter for one of the largest chiropters colony in the country, (Fig. 2).

A direct consequence for the presence of this colony is the accumulation (on the floor of the southern gallery) of a large quantity of guano. A probe drilled by POVARĂ *et al.* (1972) at a depth of 25 m failed to reach the lythic floor.

The samples we have drawn, therefore, come from the upper layer of the guano deposit, and should be rightfully considered to be more recent compared to those dated by CARBONNEL *et al.* (1999) (using $C^{14}$ methods) as being 7600 y.o. at 2.5 m deep, and 2740 y.o. at 1.2 m deep. The mineral association evidenced heretofore is made of hydroxylapatite, brushite, ardealite, gypsum and quartz.

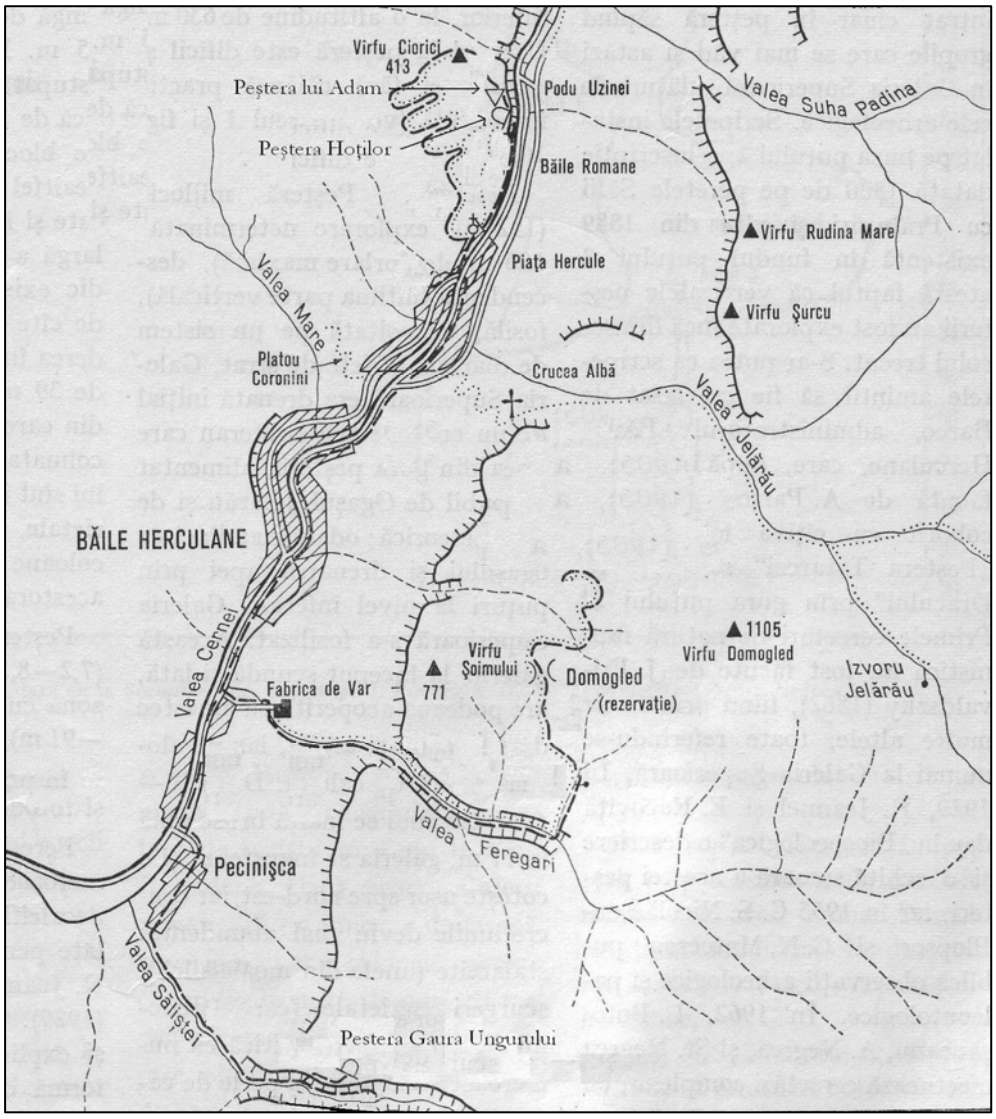


Fig. 1 – Site area Herculane Spa. Location of the caves.
(After Bleahu *et al*., 1976).

**1.1. Hydroxylapatite, $Ca_5(PO4)_3(OH)$** is the most abundant mineral, represented by crusts of creamy white consistence, less frequently ochre, and which often coats the limestone debris in the guano layer, while nodular formations or bony, digested fragments are rarer.

The diffractometry assay evidenced a high degree of crystallinity; the reticular distances, both measured and calculated, the relative intensities and the

Miller indices (hkl) for the reflexes attributed univocally to hydroxylapatite in two representative samples from the Peştera lui Adam (Cave) are shown in Table 1.

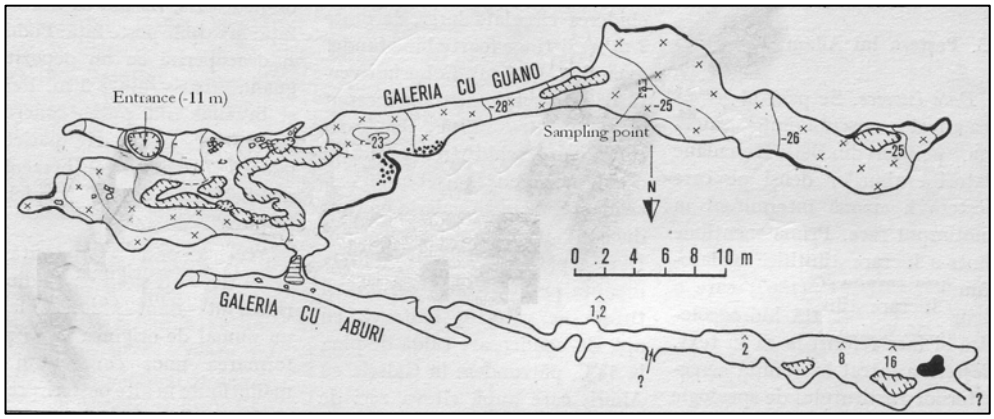


Fig. 2 – Peştera lui Adam. Sketch; location of the sampling point.

(Map modified after Povară *et al*., 1972).

*Table 1*

X-ray diffractometric data obtained from hydroxylapatite powders from the Peştera lui Adam

| No. | Sample PAA 4 A | | | Sample PAA 5 B | | | (hkl) |
|---|---|---|---|---|---|---|---|
| | $d_{meas.}$ (Å) | $d_{calc.}$ (Å) | $I / I_0$ | $d_{meas.}$ (Å) | $d_{calc.}$ (Å) | $I / I_0$ | |
| 1 | 4,0515 | 4,0776 | 7 | 4,0917 | 4,0807 | 7 | (200) |
| 2 | – | – | – | 3,8668 | 3,8868 | 7 | (111) |
| 3 | 3,4355 | 3,4391 | 61 | 3,4325 | 3,4377 | 57 | (002) |
| 4 | 3,1649 | 3,1689 | 9 | 3,1558 | 3,1681 | 12 | (102) |
| 5 | 3,0709 | 3,0823 | 14 | 3,0863 | 3,0847 | 13 | (210) |
| 6 | 2,8018 | 2,8128 | 100 | 2,8112 | 2,8144 | 100 | (211) |
| 7 | 2,7759 | 2,7772 | 76 | 2,7807 | 2,7772 | 85 | (112) |
| 8 | 2,7069 | 2,7184 | 53 | 2,7182 | 2,7204 | 63 | (300) |
| 9 | 2,2905 | 2,2954 | 11 | 2,2825 | 2,2959 | 15 | (212) |
| 10 | 2,2601 | 2,2619 | 15 | 2,2592 | 2,2635 | 27 | (130) |
| 11 | 2,0569 | 2,0613 | 10 | 2,0508 | 2,0610 | 8 | (113) |
| 12 | 2,0008 | 1,9985 | 15 | 1,9992 | 1,9983 | 8 | (203) |
| 13 | 1,9385 | 1,9426 | 38 | 1,9430 | 1,9434 | 33 | (222) |
| 14 | 1,8881 | 1,8898 | 18 | 1,8921 | 1,8905 | 23 | (132) |
| 15 | 1,8392 | 1,8396 | 33 | 1,8400 | 1,8396 | 36 | (213) |
| 16 | 1,8153 | 1,8053 | 12 | – | – | – | (321) |
| 17 | 1,7972 | 1,7796 | 15 | 1,7821 | 1,7809 | 10 | (410) |
| 18 | 1,7534 | 1,7538 | 15 | 1,7504 | 1,7546 | 13 | (402) |
| 19 | 1,7206 | 1,7229 | 21 | 1,7196 | 1,7240 | 25 | (141) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 20 | 1,7019 | 1,7196 | 3 | 1,7196 | 1,7189 | 25 | (004) |
| 21 | 1,6713 | 1,6826 | 5 | 1,6797 | 1,6820 | 6 | (104) |
| 22 | 1,5837 | 1,5870 | 4 | – | – | – | (501) |
| 23 | 1,5837 | 1,5805 | 4 | – | – | – | (412) |
| 24 | 1,5765 | 1,5695 | 6 | 1,5728 | 1,5706 | 7 | (330) |
| 25 | 1,5410 | 1,5410 | 32 | 1,5487 | 1,5423 | 4 | (240) |
| 26 | 1,4707 | 1,4737 | 12 | 1,4737 | 1,4745 | 7 | (502) |
| 27 | 1,4525 | 1,4532 | 7 | 1,4511 | 1,4531 | 21 | (304) |
| 28 | 1,3540 | 1,3564 | 4 | 1,3579 | 1,3560 | 2 | (105) |
| 29 | – | – | – | 1,3488 | 1,3484 | 5 | (105) |
| 30 | 1,3282 | 1,3290 | 6 | 1,3271 | 1,3295 | 4 | (503) |
| 31 | 1,3150 | 1,3145 | 9 | 1,3160 | 1,3146 | 10 | (404) |
| 32 | 1,3014 | 1,3035 | 7 | 1,3013 | 1,3031 | 6 | (205) |
| 33 | 1,2325 | 1,2343 | 12 | 1,2343 | 1,2348 | 4 | (513) |
| 34 | 1,2221 | 1,2208 | 5 | 1,2221 | 1,2216 | 9 | (252) |
| 35 | 1,1753 | 1,1752 | 6 | 1,1764 | 1,1752 | 5 | (135) |
| 36 | 1,1432 | 1,1464 | 9 | – | – | – | (006) |
| 37 | 1,1156 | 1,1150 | 10 | 1,1162 | 1,1153 | 5 | (514) |
| 38 | 1,1156 | 1,1149 | 10 | 1,1162 | 1,1153 | 10 | (116) |
| 39 | – | – | – | 1,1040 | 1,1041 | 6 | (352) |

Parameters for the elemental cells calculated by refinement using the least-square method on the two samples (Cu *Kα* radiation filtered through *Ni* = 1.54056 Å, $2\theta = 10 - 88^0$, number of refinement cycles: 3, 6, 4) are:

– α (Å) = 9.417(3), *c* (Å) = 6.878 (3), *V* (Å³) = 582.2 (3), n $^{(1)}$ = 4, N $^{(2)}$ = 31, I.C. $^{(3)}$ = 0.053 (for the PAA 4A sample) and,

– α (Å) = 9.424 (2), *c* (Å) = 6.875 (3), *V* (Å³) = 528.8 (3), n $^{(1)}$ = 3, N $^{(2)}$ = 62, I.C. $^{(3)}$ = 0.047 (for the PAA 5B sample).

These are close to those determined by BRUNET *et al.* (1999) for the stoechiometric hydroxylapatite: α = 9.421 (2) Å, *c* = 6.882 (3) Å

**1.2. The Ardealite, $Ca_2(PO_3OH)$ SO4 . $4H_2O$,** appears frequently in powder-like state together with gypsum from which it is nevertheless distinct due to its creamy-white color and a less evident shine, on the hydroxylapatite crusts.

The identification of the mineral was performed exclusively by diffractometric techniques, after obtaining relatively pure separates. The measured and calculated inter-reticular distances, the Miller indices and the relative intensities for the main diffractometric reflexes are given in the Table 2 for two representative ardealite samples.

The parameters for the elemental cells computed after "n" refinement cycles using the least squares method, on the basis of "N" diffractometric reflexes from the value interval 2θ ranging from $10^0$ and $90^0$ and univocally attributed to ardealite (Cu *Kα,* filtered by Ni, λ = 1.54056 Å, where the number of cycles was respectively 3, 4, 7) are:

– *a* (Å) = 5.716 (2), *b* (Å) = 40.985 (10), *c* (Å) = 6.261 (3), $\beta^{(0)}$ = 117.16 (2) *V* (Å³) = 986.8 (5), n $^{(1)}$ = 4, N $^{(2)}$ = 88,

– *a* (Å) = 5.719 (2), *b* (Å) = 30.967 (9), *c* (Å) = 6.250 (2), $\beta^{(0)}$ = 117.12 (2) *V* (Å³) = 984.7 (4), n $^{(1)}$ = 7, N $^{(2)}$ = 93

These values are comparable to those calculated by SAKAE *et al.* (1978) for synthetic ardealite (*a* = 5.721 (5) Å, *b* = 30.992 (5) Å, *c* = 6.250 (4) Å and *β* = 117.26 (6)$^0$

*Table 2*

X-ray diffractometric data obtained from ardealite powders from the Peştera lui Adam (Cave)

| No. | Sample PAA 6 A | | | Sample PAA 6 B | | | (hkl) |
|---|---|---|---|---|---|---|---|
| | $d_{meas.}$ (Å) | $d_{calc.}$ (Å) | $I / I_0$ | $d_{meas.}$ (Å) | $d_{calc.}$ (Å) | $I / I_0$ | |
| 1 | 7,6868 | 7,7464 | 100 | 7,6765 | 7,7418 | 100 | (040) |
| 2 | 4,2507 | – | 40 | 4,2509 | – | 60 | – |
| 3 | 4,1292 | – | 7 | 4,1311 | – | 6 | – |
| 4 | 3,9164 | 3,9314 | 4 | 3,9391 | 3,9319 | 4 | (–151) |
| 5 | 3,9164 | 3,9313 | 4 | 3,9391 | 3,9294 | 4 | (150) |
| 6 | 3,8610 | 3,8732 | 24 | 3,8633 | 3,8709 | 28 | (080) |
| 7 | 3,7941 | 3,7874 | 4 | 3,7919 | 3,7829 | 10 | (061) |
| 8 | 3,3270 | 3,3390 | 6 | 3,3355 | 3,3383 | 75 | (–171) |
| 9 | 3,3270 | 3,3389 | 6 | 3,3355 | 3,3372 | 75 | (170) |
| 10 | – | – | – | 3,1704 | 3,1769 | 13 | (081) |
| 11 | 2,9732 | 2,9819 | 6 | 2,9936 | 2,9796 | 11 | (131) |
| 12 | – | – | – | 2,8009 | 2,8117 | 34 | (–221) |
| 13 | 2,5378 | 2,5429 | 17 | – | – | – | (200) |
| 14 | 2,4419 | 2,4518 | 19 | 2,4452 | 2,4478 | 15 | (062) |
| 15 | 2,1567 | 2,1582 | 3 | 2,1538 | 2,1573 | 4 | (–1.13.1) |
| 16 | 2,1567 | 2,1581 | 3 | 2,1538 | 2,1570 | 4 | (1.13.0) |
| 17 | – | – | – | 2,0685 | 2,0690 | 20 | (0.10.2) |
| 18 | – | – | – | 1,9767 | 1,9779 | 1 | (–223) |
| 19 | 1,9657 | 1,9784 | 4 | 1,9767 | 1,9761 | 1 | (221) |
| 20 | 1,9308 | 1,9366 | 11 | 1,9370 | 1,9355 | 15 | (0.16.0) |
| 21 | 1,8917 | 1,8937 | 4 | 1,8959 | 1,8916 | 10 | (1.13.1) |
| 22 | 1,8917 | 1,8928 | 4 | 1,8959 | 1,8914 | 10 | (0.12.2) |
| 23 | 1,8729 | 1,8798 | 5 | 1,8728 | 1,8776 | 9 | (172) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 24 | 1,8617 | 1,8608 | 5 | 1,8568 | 1,8587 | 9 | (261) |
| 25 | 1,6953 | 1,6928 | 5 | 1,6881 | 1,6920 | 10 | (–313) |
| 26 | 1,6953 | 1,6927 | 5 | – | – | – | (310) |
| 27 | 1,6668 | 1,6695 | 5 | 1,6692 | 1,6696 | 14 | (–2.14.2) |
| 28 | 1,5847 | 1,5832 | 3 | 1,5845 | 1,5835 | 8 | (–373) |
| 29 | 1,5692 | 1,5656 | 3 | 1,5643 | 1,5640 | 8 | (–1.13.3) |
| 30 | 1,5417 | 1,5407 | 9 | 1,5409 | 1,5403 | 13 | (–2.16.2) |
| 31 | 1,5417 | 1,5406 | 9 | 1,5409 | 1,5399 | 13 | (2.16.0) |
| 32 | 1,4953 | 1,4926 | 2 | 1,4904 | 1,4916 | 13 | (0.20.1) |
| 33 | 1,4191 | 1,4171 | 2 | 1,4160 | 1,4163 | 4 | (–1.21.0) |
| 34 | – | – | – | 1,4064 | 1,4059 | 9 | (–442) |
| 35 | – | – | – | 1,3691 | 1,3685 | 9 | (–1.17.3) |
| 36 | 1,3490 | 1,3469 | 3 | 1,3496 | 1,3450 | 6 | (–1.11.4) |
| 37 | 1,3490 | 1,3468 | 3 | 1,3496 | 1,3446 | 6 | (1.11.3) |
| 38 | 1,3392 | 1,3370 | 2 | – | – | – | (–463) |
| 39 | 1,3392 | 1,3369 | 2 | – | – | – | (–461) |
| 40 | 1,3331 | 1,3334 | 2 | 1,3338 | 1,3326 | 10 | (1.21.1) |
| 41 | 1,3242 | 1,3231 | 3 | 1,3216 | 1,3223 | 10 | (–2.20.2) |
| 42 | – | – | – | 1,2974 | 1,2903 | 4 | (–4.10.2) |
| 43 | 1,2884 | 1,2880 | 3 | 1,2869 | 1,2877 | 9 | (–3.11.4) |
| 44 | 1,2818 | 1,2826 | 2 | 1,2801 | 1,2814 | 8 | (–1.19.3) |
| 45 | 1,2723 | 1,2714 | 8 | 1,2742 | 1,2719 | 10 | (400) |
| 46 | – | – | – | 1,2554 | 1,2558 | 10 | (0.22.2) |
| 47 | – | – | – | 1,2554 | 1,2541 | 10 | (–444) |
| 48 | 1,2513 | 1,2503 | 5 | 1,2554 | 1,2506 | 10 | (–4.12.2) |

**1.3. Brushite, $CaH(PO_4) \cdot 2H_2O$** was identified as being totally isolated in the phosphate sediment included in this analysis, where it is present in the form of micro-crystalline powdery aggregates, of bright white texture with a *specific* shine.

Because of the mixing with ardealite we could not obtain pure enough separates which would have allowed the recording of reproducible diffractograms. However, the reflex doubling around the 7.7 Å mark confirms a mixture of ardealite, brushite and quartz, with a possible indexing of brushite using diffractometric lines. The elemental cells values, obtained through refinement using the least squares method for the 2θ interval, between $5^0$ and $90^0$, (Cu *Kα,* $\lambda$ = 1.5406 Å) attributed to brushite are $a$ = 5.803 (2) Å, $b$ = 15.179 (7) Å, $c$ = 6.261 (4) Å, $\beta = 116.12\ (3)^0$.

The main contrast with numbers given by BEEVERS (1958) or CURRY and JONES (1971) for the stoechiometric brushite [$a$ = 5.812 (2) Å, $b$ = 15.180 (3) Å, $c$ = 6.239 (2) Å, $\beta = 116.43\ (3)^0$] is mainly due the interference with ardealite lines included in the sample used for analysis.

**1.4. Gypsum, $CaSO_4 \cdot 2H_20$** appears in the shape of efflorescent layers associated with crust-like ardealite sediments, from which it's distinct because of its shiny white color. Table 3 contains both measured and calculated inter-reticular distances, the relative intensities and Miller indices (hkl) for the main diffractometric reflexes recorded on a representative sample of gypsum from Peştera lui Adam (Cave).

*Table 3*

X-ray diffractometric data obtained for gypsum powder from the Peştera lui Adam (Cave)

| No. | Sample PAA 6 B | | | (hkl) | Nr. crt. | Sample PAA 6 B | | | (hkl) |
|---|---|---|---|---|---|---|---|---|---|
| | $d_{meas.}$ (Å) | $d_{calc.}$ (Å) | $I / I_0$ | (hkl) | | $d_{meas.}$ (Å) | $d_{calc.}$ (Å) | $I / I_0$ | (hkl) |
| 1 | 7,6765 | 7,5868 | 79 | (020) | 47 | 1,4975 | 1,4947 | 10 | (–361) |
| 2 | 4,7901 | 4,7492 | 3 | (110) | 48 | 1,4842 | 1,4857 | 6 | (–314) |
| 3 | 4,2539 | 4,2771 | 100 | (–121) | 49 | 1,4379 | 1,4417 | 5 | (143) |
| 4 | 3,7919 | 3,7934 | 8 | (040) | 50 | 1,4379 | 1,4352 | 5 | (073) |
| 5 | 3,7919 | 3,7963 | 8 | (031) | 51 | 1,4379 | 1,4363 | 5 | (004) |
| 6 | 3,1704 | 3,1698 | 10 | (–112) | 52 | 1,4297 | 1,4262 | 5 | (–183) |
| 7 | 3,0578 | 3,0602 | 73 | (–141) | 53 | 1,4160 | 1,4183 | 4 | (–402) |
| 8 | 2,8722 | 2,8788 | 41 | (121) | 54 | 1,4064 | 1,4050 | 7 | (321) |
| 9 | 2,8722 | 2,8726 | 41 | (002) | 55 | 1,3943 | 1,3942 | 4 | (–422) |
| 10 | 2,7164 | 2,7290 | 15 | (–132) | 56 | 1,3862 | 1,3855 | 6 | (–413) |
| 11 | 2,5986 | 2,5943 | 3 | (150) | 57 | 1,3561 | 1,3576 | 8 | (–411) |
| 12 | 2,5323 | 2,5289 | 7 | (060) | 58 | 1,3265 | 1,3254 | 8 | (–381) |
| 13 | 2,4973 | 2,5002 | 18 | (200) | 59 | 1,3265 | 1,3269 | 8 | (163) |
| 14 | 2,4452 | 2,4504 | 12 | (–222) | 60 | 1,3265 | 1,3251 | 8 | (262) |
| 15 | 2,4027 | 2,4058 | 9 | (141) | 61 | 1,3216 | 1,3213 | 10 | (370) |
| 16 | 2,3700 | 2,3746 | 6 | (220) | 62 | 1,3115 | 1,3142 | 7 | (192) |
| 17 | 2,2991 | 2,2901 | 4 | (042) | 63 | 1,2974 | 1,3000 | 3 | (–215) |
| 18 | 2,2089 | 2,2153 | 7 | (–152) | 64 | 1,2974 | 1,2946 | 3 | (–404) |
| 19 | 2,0862 | 2,0876 | 13 | (240) | 65 | 1,2869 | 1,2851 | 7 | (–174) |
| 20 | 2,0685 | 2,0783 | 16 | (–251) | 66 | 1,2801 | 1,2824 | 6 | (291) |
| 21 | 2,0319 | 2,0281 | 4 | (071) | 67 | 1,2742 | 1,2766 | 8 | (–383) |
| 22 | 1,9370 | 1,9380 | 12 | (132) | 68 | 1,2742 | 1,2761 | 8 | (–424) |
| 23 | 1,8959 | 1,8982 | 8 | (062) | 69 | 1,2554 | 1,2550 | 8 | (–392) |
| 24 | 1,8959 | 1,9000 | 8 | (013) | 70 | 1,2489 | 1,2502 | 6 | (–325) |
| 25 | 1,8728 | 1,8793 | 7 | (–143) | 71 | 1,2489 | 1,2501 | 6 | (400) |
| 26 | 1,8353 | 1,8400 | 7 | (231) | 72 | 1,2489 | 1,2489 | 6 | (064) |
| 27 | 1,7844 | 1,7810 | 9 | (–181) | 73 | 1,2334 | 1,2335 | 8 | (420) |
| 28 | 1,7760 | 1,7780 | 8 | (260) | 74 | 1,2334 | 1,2321 | 8 | (–284) |
| 29 | 1,7647 | 1,7616 | 3 | (–332) | 75 | 1,2290 | 1,2295 | 5 | (–374) |
| 30 | 1,7282 | 1,7258 | 5 | (152) | 76 | 1,2290 | 1,2284 | 5 | (–1.12.1) |
| 31 | 1,7282 | 1,7224 | 5 | (–271) | 77 | 1,2235 | 1,2252 | 6 | (–444) |
| 32 | 1,7084 | 1,7069 | 8 | (–253) | 78 | 1,2208 | 1,2220 | 5 | (233) |
| 33 | 1,6881 | 1,6831 | 5 | (–323) | 79 | 1,2095 | 1,2096 | 6 | (312) |
| 34 | 1,6692 | 1,6649 | 11 | (–341) | 80 | 1,2041 | 1,2042 | 7 | (183) |
| 35 | 1,6444 | 1,6439 | 5 | (–163) | 81 | 1,2041 | 1,2029 | 7 | (282) |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 36 | 1,5942 | 1,5977 | 10 | (–352) | | 82 | 1,2041 | 1,2022 | 7 | (–345) |
| 37 | 1,5942 | 1,5976 | 10 | (190) | | 83 | 1,1981 | 1,1988 | 4 | (134) |
| 38 | 1,5845 | 1,5828 | 7 | (082) | | 84 | 1,1941 | 1,1936 | 6 | (–145) |
| 39 | 1,5845 | 1,5831 | 7 | (330) | | 85 | 1,1889 | 1,1873 | 7 | (440) |
| 40 | 1,5746 | 1,5711 | 12 | (–343) | | 86 | 1,1707 | 1,1714 | 3 | (1.12.1) |
| 41 | 1,5321 | 1,5301 | 6 | (–282) | | 87 | 1,1707 | 1,1709 | 3 | (–473) |
| 42 | 1,5235 | 1,5267 | 8 | (123) | | 88 | 1,1629 | 1,1631 | 5 | (253) |
| 43 | 1,5235 | 1,5218 | 8 | (–134) | | 89 | 1,1629 | 1,1612 | 5 | (–415) |
| 44 | 1,5145 | 1,5174 | 8 | (0.10.0) | | 90 | 1,1571 | 1,1573 | 6 | (0.12.2) |
| 45 | 1,5145 | 1,5111 | 8 | (280) | | 91 | 1,1514 | 1,1526 | 5 | (–464) |
| 46 | 1,4975 | 1,4949 | 10 | (–273) | | 92 | 1,1514 | 1,1526 | 5 | (1.11.2) |

The elemental cells parameters obtained after 8 refinement cycles using the least-squares method, on the basis of 103 diffractometric reflexes from the values interval 2θ ranging from $5^0$ to $90^0$ (Cu *Kα*, $\lambda$ = 1.54056 Å) are $\alpha$ = 5.679 (2) Å, $b$ = 15.174 (5) Å, $c$ = 6.525 (2) Å and $\beta$ = 118.29 (2) $^0$. Values are close to those calculated for the Hampshire gypsum, in the UK, by PEDERSEN and SEMMINGSEN (1982), [$\alpha$ = 5.679 (5) Å, $b$ = 15.202 (14) Å, $c$ = 6.522 (6) Å, $\beta$ = 118.43(4) $^0$].

**1.5. Quartz, *αSiO₂*** is a common occurrence, in association with hydroxylapatite, where it appears in the shape of milky-white granules or pellets.

The elemental cells parameters for two representative samples of α-quartz taken from Peştera lui Adam, established after "n" refinement cycles using the least-squares method, starting from "N" diffractometric reflexes from the values interval 2θ ranging from 5 to 90° (Cu *Kα*, $\lambda$ = 1.54056 Å), attributed univocally to quartz, are as following:

– Sample PAA 5A: $\alpha$ = 4.914 (18) Å, $c$ = 5.499 (34) Å, $V$ = 113.0(6) Å$^3$, (n = 3, N = 19)

– Sample PAA 5B: $\alpha$ = 4.912 (2) Å, $c$ = 5.405 (5) Å, $V$ = 113.0(1) Å$^3$, (n = 3, N = 19).

In both cases the calculated parameters are relatively close to those determined by WILL *et al.* (1988) for the stoechiometric $\alpha$ – quartz [$\alpha$ = 4.91239(4) Å, $c$ = 5.40385 (7) Å and $V$ = 112.933 Å$^3$].

## 2. GAURA UNGURULUI CAVE

This cavity, also known as the Gaura Ungurului from Pecinişca Cave has a total gallery span of 196 m (see Fig. 3), deep down into the Malm-Neocomian limestone of the Domogled massive, east of Pecinişca, a community neighboring Băile Herculane to the south.

Due to its easy access via four entrances, all situated at approximately 20 m high in relation to the western wall of the Pecinişca Gorge, (which cuts through the

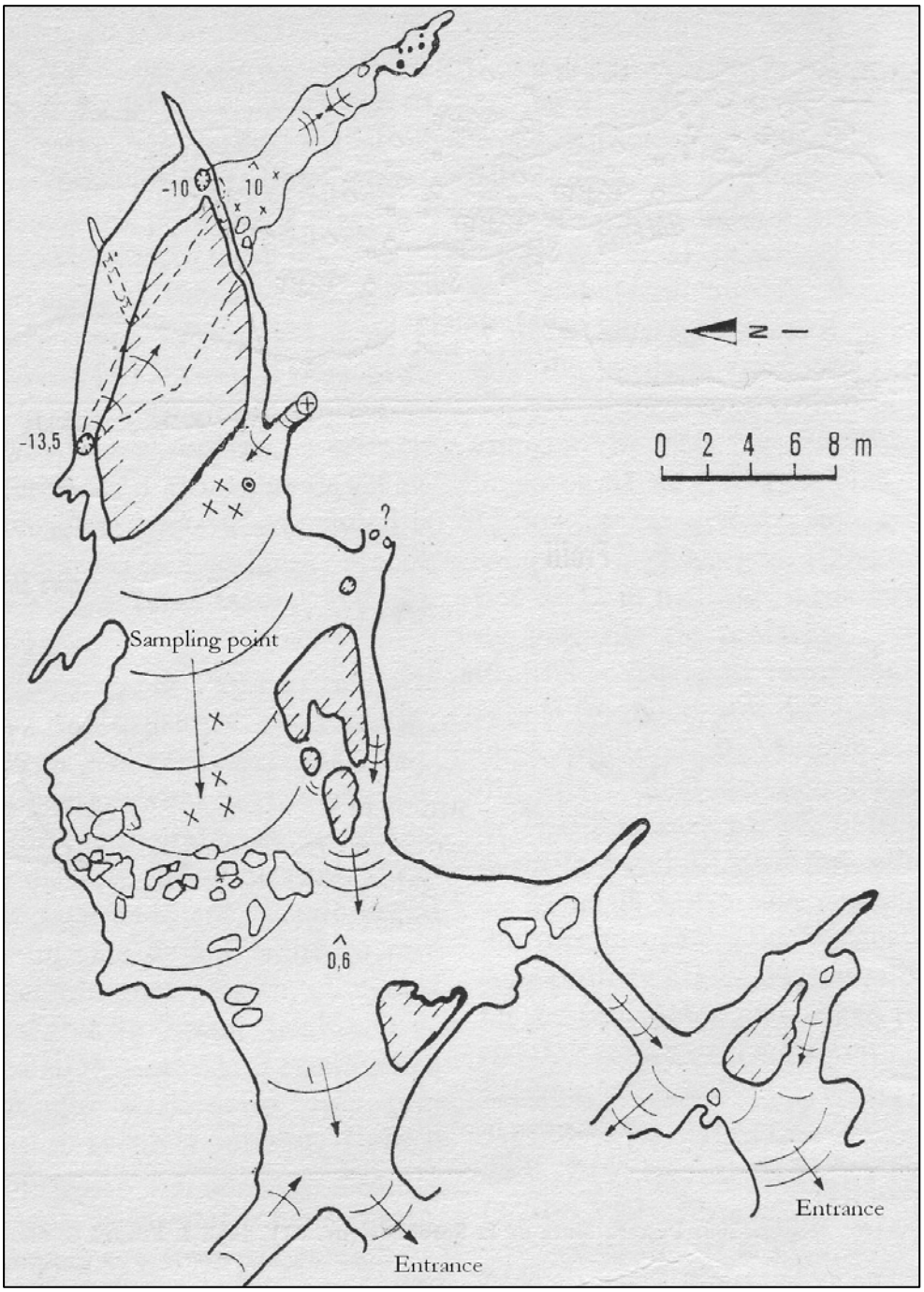


Fig. 3 – Gaura Ungurului Cave; location of the sampling point.
(Map modified after Botoşăneanu *et al*., 1967).

Salištea Valley), this cave was explored by biologists since the beginning of the 20th century (MEHELY, 1900). We drew mineralogical samples from the hall directly communicating with all the entrances, whose floor is basically covered in its entirety by a thick layer of guano. Our analysis evidenced the presence of mainly taranakite, and to a much lesser extent that of quartz.

**2.1. Taranakite, $K_3Al_5(HPO_4)$ . $18H_2O$,** represents the essential mineral found in our samples. It appears in guano deposits as streaks of white or creamy-white matter placed at the interface with detritic levels in *terra rosa* facies.

X-ray diffractograms on taranakite powders show well defined peaks; values "d" for the inter-reticular distances both calculated and measured, the relative intensities $I/I_0$ and Miller indices (hkl) corresponding to two significant samples, are shown in Table 4. The elemental cells parameters obtained for the two samples using refinement through least-squares method starting from sets of 121, respectively 99 diffractometric reflexes from the 2θ interval ranging from $5^0$ to $86^0$ (Fe$K\alpha$, filtered with Mn, $\lambda$ = 1.93735 Å) are:

– sample PGU 8A: $a$ = 8.673(2) Å, $c$ = 94.80(3) Å, $V$ = 6176 (3) Å$^3$,$a$:$c$ = 0.091:1;

– sample PGU 12A: $a$ = 8.646(2) Å, $c$ = 94.67 (4) Å, $V$ = 6128 (3) Å$^3$, $a$:$c$ = 0.091:1

Numbers are similar to those supplied by FIORE and LAVIANO (1991) for the Apulia Cave in Italy ($a$ = 8.676(6) Å, $c$ = 95.56(8) Å).

*Table 4*

X-ray diffractometric data obtained for significant samples of taranakite in the Gaura Ungurului Cave

| No. | Sample PGU 8 A | | | Sample PGU 12 A | | | (hkl) |
|---|---|---|---|---|---|---|---|
| | $d_{meas.}$ Å | $d_{calc.}$ Å | $I / I_0$ | $d_{meas.}$ Å | $d_{calc.}$ Å | $I / I_0$ | |
| 1 | 15,7098 | 15,8007 | 100 | 15,6939 | 15,7741 | 100 | (006) |
| 2 | 7,9777 | 7,9003 | 29 | 7,8725 | 7,8871 | 35 | (0.0.12) |
| 3 | 7,3450 | 7,4183 | 38 | 7,3860 | 7,6987 | 34 | (012) |
| 4 | 7,1007 | 7,1599 | 10 | 7,1383 | 7,1415 | 7 | (104) |
| 5 | 5,8449 | 5,8872 | 32 | 5,8718 | 5,8737 | 28 | (1.0.10) |
| 6 | 5,0025 | 5,0294 | 8 | 5,0108 | 5,0187 | 9 | (0.1.14) |
| 7 | 4,6538 | 4,6520 | 9 | 4,6426 | 4,6424 | 10 | (1.0.16) |
| 8 | 4,3329 | 4,3364 | 18 | 4,3207 | 4,3249 | 15 | (110) |
| 9 | 4,2872 | 4,2961 | 29 | 4,2841 | 4,2848 | 26 | (113) |
| 10 | 4,1830 | 4,1816 | 6 | 4,1740 | 4,1709 | 4 | (116) |
| 11 | 4,0025 | 4,0099 | 12 | 3,9927 | 3,9998 | 13 | (119) |
| 12 | 3,7976 | 3,8015 | 89 | 3,7850 | 3,7921 | 85 | (1.1.12) |
| 13 | 3,7338 | 3,7378 | 24 | 3,7328 | 3,7306 | 26 | (1.0.22) |
| 14 | 3,5748 | 3,5758 | 49 | 3,5633 | 3,5673 | 46 | (1.1.15) |
| 15 | 3,3481 | 3,3477 | 24 | 3,3402 | 3,3401 | 24 | (1.1.18) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 16 | 3,2754 | 3,2842 | 29 | 3,2726 | 3,2762 | 26 | (2.0.14) |
| 17 | 3,1755 | 3,1720 | 19 | 3,1670 | 3,1644 | 20 | (0.2.16) |
| 18 | 3,1298 | 3,1274 | 71 | 3,1225 | 3,1205 | 76 | (1.1.21) |
| 19 | 2,9478 | 2,9436 | 16 | 2,9324 | 3,9369 | 17 | (2.0.20) |
| 20 | 2,9191 | 2,9202 | 7 | 2,9073 | 2,9140 | 8 | (1.1.24) |
| 21 | 2,7730 | 2,7785 | 12 | 2,7689 | 2,7711 | 12 | (217) |
| 22 | 2,7230 | 2,7289 | 22 | 2,7183 | 2,7232 | 26 | (1.1.27) |
| 23 | 2,7230 | 2,7195 | 22 | 2,7131 | 2,7125 | 21 | (2.1.10) |
| 24 | 2,6127 | 2,6161 | 31 | 2,6055 | 2,6104 | 34 | (2.0.26) |
| 25 | 2,5589 | 2,5602 | 11 | 2,5521 | 2,5538 | 12 | (2.1.16) |
| 26 | 2,5260 | 2,5299 | 7 | 2,5224 | 2,5237 | 7 | (1.2.17) |
| 27 | 2,4698 | 2,4728 | 4 | 2,4659 | 2,4662 | 5 | (306) |
| 28 | 2,4335 | 2,4355 | 1 | 2,4255 | 2,4296 | 1 | (1.2.20) |
| 29 | 2,3835 | 2,3866 | 23 | 2,3812 | 2,3805 | 23 | (0.3.12) |
| 30 | 2,3373 | 2,3380 | 6 | 2,3318 | 2,3325 | 7 | (1.2.23) |
| 31 | 2,2553 | 2,2602 | 7 | 2,2525 | 2,2562 | 10 | (1.0.40) |
| 32 | 2,2553 | 2,2572 | 7 | 2,2525 | 2,2534 | 10 | (0.0.42) |
| 33 | 2,1409 | 2,1435 | 7 | 2,1392 | 2,1387 | 7 | (1.2.29) |
| 34 | 2,1139 | 2,1147 | 4 | 2,1091 | 2,1096 | 4 | (3.0.24) |
| 35 | 2,0833 | 2,0826 | 8 | 2,0780 | 2,0771 | 7 | (131) |
| 36 | 2,0343 | 2,0346 | 5 | 2,0298 | 2,0293 | 5 | (1.3.10) |
| 37 | 1,8998 | 1,9007 | 7 | 1,8987 | 1,8961 | 6 | (2.2.24) |
| 38 | 1,8998 | 1,9021 | 7 | 1,8987 | 1,8980 | 6 | (2.1.37) |
| 39 | 1,8428 | 1,8419 | 3 | 1,8389 | 1,8371 | 4 | (4.0.10) |
| 40 | 1,8428 | 1,8448 | 3 | 1,8389 | 1,8404 | 4 | (2.2.27) |
| 41 | 1,7969 | 1,7974 | 6 | 1,7959 | 1,7941 | 10 | (1.1.48) |
| 42 | 1,7744 | 1,7742 | 7 | 1,7722 | 1,7754 | 7 | (1.3.28) |
| 43 | 1,7409 | 1,7413 | 3 | 1,7381 | 1,7377 | 5 | (2.1.43) |
| 44 | 1,6776 | 1,6765 | 3 | 1,6751 | 1,6729 | 6 | (0.3.42) |
| 45 | 1,6406 | 1,6390 | 7 | 1,6389 | 1,6346 | 7 | (410) |
| 46 | 1,6406 | 1,6368 | 7 | 1,6389 | 1,6325 | 7 | (143) |
| 47 | 1,6204 | 1,6194 | 5 | 1,6197 | 1,6153 | 6 | (2.3.20) |
| 48 | 1,5661 | 1,5650 | 3 | 1,5642 | 1,5609 | 3 | (1.4.18) |
| 49 | 1,5661 | 1,5647 | 3 | 1,5642 | 1,5612 | 3 | (1.3.40) |
| 50 | 1,5148 | 1,5142 | 2 | 1,5148 | 1,5108 | 1 | (1.3.43) |
| 51 | 1,4858 | 1,4846 | 2 | 1,4842 | 1,4819 | 3 | (1.1.60) |
| 52 | 1,4325 | 1,4320 | 1 | 1,4318 | 1,4283 | 2 | (5.0.20) |
| 53 | 1,4325 | 1,4320 | 1 | 1,4318 | 1,4283 | 2 | (339) |
| 54 | 1,4228 | 1,4217 | 3 | 1,4158 | 1,4191 | 7 | (1.1.63) |

**2.2. Quartz, *αSiO₂*** is practically omnipresent in association with the taranakite aggregates, in whose mass it is evidenced as coralloid aggregates.

The elemental cells values determined after "n" refinement cycles [using the least-squares method for quartz in association with the taranakite, departing from a standard number of 15 cycles attributable univocally to quartz, situated in the "d" values interval ranging from 4.3 and 1.3 Å (Fe$K\alpha$, $\lambda$ = 1.93735 Å)] are:

– sample PGU 2A: $\alpha$ = 4.905(2) Å, $c$ = 5.399(4) Å, $V$ = 112.50(9) Å$^3$, (n = 3)
– sample PGU 8B: $\alpha$ = 4.907(1) Å, $c$ = 5.402(3) Å, $V$ = 112.64(6) Å$^3$, (n = 4).

These are reasonably close to those determined by WILL *et al* (1988) for the stoechiometric $\alpha$ – quartz [$\alpha$ = 4.91239(4) Å, $c$ = 5.40385(7) Å, $V$ = 112.933 Å$^3$].

## 3. HOŢILOR CAVE IN BĂILE HERCULANE (THE GROTA HAIDUCILOR CAVE)

The Hoţilor Cave in Băile Herculane is situated on the western slope of the Cerna Gorge, at approximately 25 m from the valley thalweg, dug in the same Malm-Neocomian limestone facies.

The total length of the cavity is only 143 m (Fig. 4), of which only the central hall presented interest to us. From here we took samples from the stratified levels opened by an old archaeological site that were later analyzed through X-ray diffractometry. The analysis evidenced a main mineral, and a subordinate one: hydroxylapatite and $\alpha$-quartz.

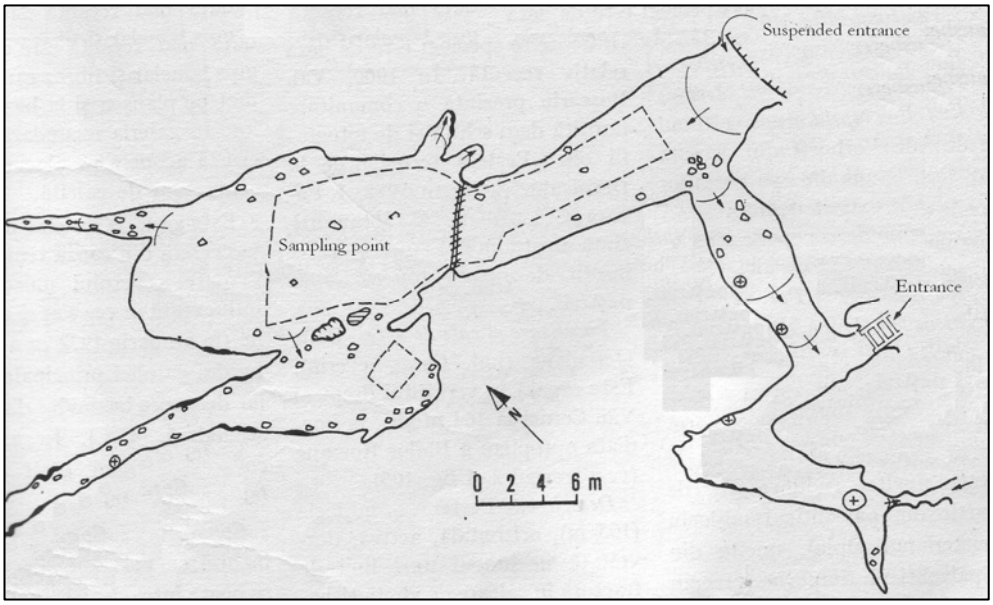


Fig. 4 – Hoţilor Cave; location of the sampling point.
(Map modified after Botoşăneanu *et al.,* 1967).

**3.1. Hydroxylapatite, $Ca_5(PO_4)_3(OH)$** appears as a yellow or ochre dull crust. It is just slightly crystallized, with crystallinity indices calculated using the

method proposed by SIMPSON (1964) higher than 0.2. The measured and calculated inter-reticular distances, the Miller indices (hkl) and the relative intensities for the main diffractometric reflexes we obtained on a representative sample taken from Hoților Cave (samples PH 2A) are presented in Table 5.

*Table 5*

X-Ray Diffractometry data obtained from a significant sample of hydroxylapatite from the Hoților Cave in Băile Herculane

| No. | Sample PH 2 A | | | (hkl) |
|---|---|---|---|---|
| | $d_{meas.}$ Å | $d_{calc.}$ Å | $I / I_0$ | |
| 1 | 5,2881 | 5,2518 | 3 | (101) |
| 2 | 3,8637 | 3,8820 | 8 | (111) |
| 3 | 3,4329 | 3,4336 | 35 | (002) |
| 4 | 3,1810 | 3,1643 | 95 | (102) |
| 5 | 2,8036 | 2,8109 | 100 | (211) |
| 6 | 2,7746 | 2,7738 | 58 | (112) |
| 7 | 2,6277 | 2,6259 | 18 | (202) |
| 8 | 1,9912 | 1,9958 | 10 | (203) |
| 9 | 1,9415 | 1,9410 | 21 | (222) |
| 10 | 1,8720 | 1,8700 | 14 | (230) |
| 11 | 1,8340 | 1,8374 | 28 | (213) |
| 12 | 1,8051 | 1,8043 | 75 | (321) |
| 13 | 1,7791 | 1,7787 | 19 | (410) |
| 14 | 1,7533 | 1,7524 | 13 | (402) |
| 15 | 1,7533 | 1,7506 | 13 | (303) |
| 16 | 1,7160 | 1,7168 | 22 | (004) |
| 17 | 1,6370 | 1,6422 | 7 | (322) |
| 18 | 1,5394 | 1,5404 | 41 | (240) |
| 19 | 1,5025 | 1,5031 | 9 | (241) |
| 20 | 1,4496 | 1,4482 | 11 | (323) |
| 21 | 1,3812 | 1,3869 | 17 | (224) |

Fe *Kα* radiation filtered with Mn (λ =1,93735 Å), $2\theta = 10^0 – 86^0$.

The elemental cells parameters determined for the above-said sample [$a$ = 9.412(5) Å, $c$ =6.867(6), $V$ = 526.9(6) Å$^3$] are relatively close to those determined for the stoechiometric hydroxylapatite by BRUNET *et al.* (1999), [$a$ = 9.421(2) Å, $c$ = 6.882(3) Å].

**3.2. Quartz, αSiO$_2$** appears in the form of crystalline aggregates of milky-white color, embedded in the hydroxylapatite crust.

The elemental cells parameters determined after three refinement cycles using the least-squares method, starting from 15 cycles attributable univocally to

quartz in an analyzed sample, lying in the interval 2θ ranging from 10 to 87° (Fe *Kα*, $\lambda$ = 1.93735 Å) are: $a$ = 4.908(2) Å, $c$ = 5.400(4) Å, $V$ = 112.64(7) Å$^3$. Numbers are relatively close to those determined by WILL *at al.* (1988) for the stoechiometric *α*-quartz ($a$ = 4.9123(4), $c$ = 5.4085 and $V$ = 112.933 Å$^3$).

The present paper adds the mineralogical data to the previous information concerning biospeleology, archaeology and thermalism (POVARĂ *et al.,* 1972, BOTOŞĂNEANU *et al.* etc.) of the caves from the Băile Herculane area.

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