

COLD SPRING WATER CHEMICAL IMPRINT IN VRANCEA REGION (SUBCARPATHIAN NAPPE, ROMANIA) FOR ASSESSING THE FLUIDS ORIGIN

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ABSTRACT

The investigated cold spring (10.4-10.9 °C) is located onto a reverse fault zone within the Subcarpathian nappe (Vrancea region). A small travertine deposit has precipitated along the stream.

The spring-water samples display an essentially calcium-bicarbonate chemical facies, indicative of a prevalently meteoric water contribution. Still significant Na and Cl concentrations - each of them amounting, when expressed as miliequivalents, to about one third of the HCO₃ concentration - also suggest mixing with a significant fraction of NaCl groundwater. Moreover, when considering the abundance of sulfate - whose concentrations, expressed as miliequivalents, amount to one quarter of the Ca concentrations - gypsum appears to be leached as well.

Gypsum leaching is also substantiated by the fact that for the majority of the trace and major elements analyzed in the travertine, the relative contents are roughly proportional to the corresponding relative contents identified in the underlying, so-called the Perchiu gypsum formation.

Overall, such inferences are in agreement with the evaporite rocks occurrences existing in the Subcarpathian nappe sedimentary sequence situated below the deposits from which the spring actually discharges.

All those lines of evidence consistently suggest that the spring-water saline component originates in formations occurring at deeper levels of the Subcarpathian nappe stratigraphic sequence.

Keywords: travertine, cold spring, trace elements, fluid evolution, Vrancea.

INTRODUCTION

Hypotheses on possible deep origins of the spring waters which discharged in the East Carpathians Bend (Vrancea) region have been extensively discussed in [1], by taking into account the concerned fluids chemical and isotopic compositions. Alternatively,

possible information which travertine deposits could provide in this respect has not been addressed, to our knowledge, so far.

Therefore, the present study represents a first attempt to investigate the mineralogy of a travertine deposit of the concerned region; further on, the major and trace element concentrations of the travertine and of the depositing cold spring-water were correlated with the corresponding concentrations in the potential host rocks of the underlying sedimentary sequence, in order to assess the fluids origin.

GEOLOGICAL SETTING

The Vrancea region as a whole consists of a system of north-south trending, thin-skinned nappes, which belong to the Carpathians orogen. The nappes emplacement has been completed during Sarmatian times [2].

Within this area (Fig. 1), the sedimentary succession of the Subcarpathian nappe has a thickness up to 3200 m ([2]) and it is made up of marine siliciclastic and evaporitic rocks of Aquitanian to lower Badenian ages.

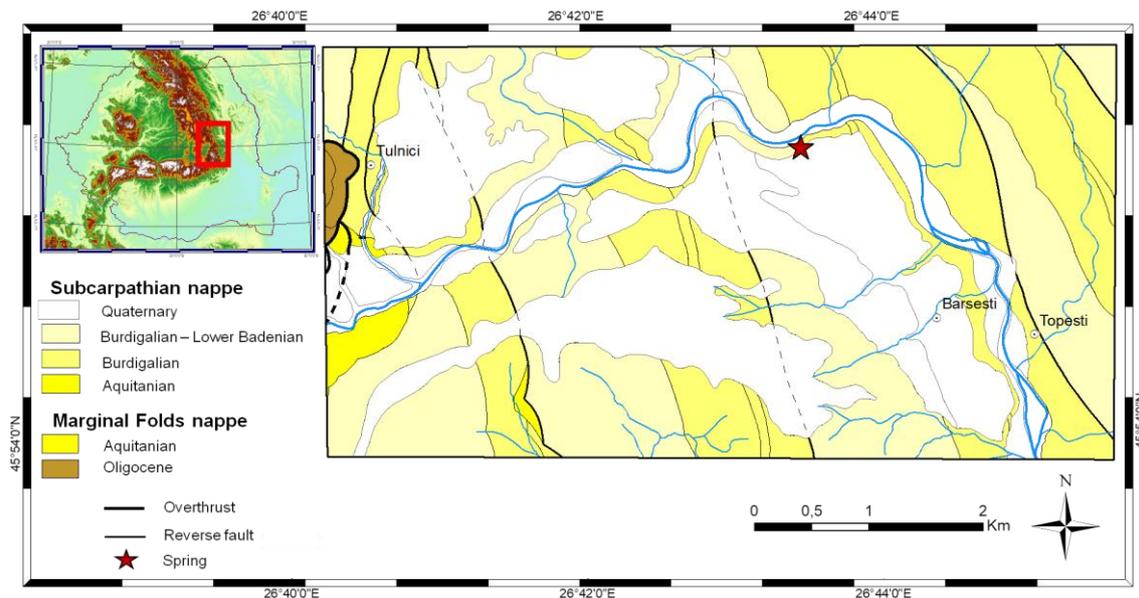


Figure 1. The location of Vrancea region within the Romanian territory (inset, after [3]) and the geological map of the Subcarpathian nappe within the studied area (modified after [2]).

The sedimentary succession starts in Aquitanian with Salt Breccia Formation, which consists of grey-black shales and marls, with levels of sandstones, microconglomerate or menilites. It is followed by three siliciclastic formations (Măgirești, Drăgugești and Bârsești Formations), which were synchronously developed during Early Burdigalian. They stand out by cyclic alternations between thick packages of well-cemented lithic quartz-lithic sandstones and polymictic microconglomerate, rarely conglomerates, and siltstones, marls and mainly red shales. The sedimentary succession continues with Perchiu Formation, which represents an evaporitic level consisting of gypsum and anhydrite, gypsum shales and thin layers of sandstones. Towards the upper part of the

Burdigalian and the beginning of the Badenian, there are Grey and Red Formations, which are composed of cyclic alternations of grey or reddish shales, marls and well-cemented sandstones. During Badenian, the sedimentary successions closes with Răchitașu Formation formed of cycling alternations of sandstones, microconglomerates, marls with globigerinae and shales, alongside which two tuff levels appear.

METHODS

For the current study, the chemical analysis of both travertine, and water samples, has been performed by the Hydrogeochemistry Laboratory of the “Emil Racoviță” Institute of Speleology in Bucharest.

The water discharged by the cold spring has been sampled in October 2015, July 2016 and September 2017. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used for determining the concentrations all constituents, except HCO_3 and SO_4^{2-} , which were analyzed by the Gran titration procedure, and argentometric titration (Mohr method), respectively. The utilized ICP-MS instrument was NexION 300S (PerkinElemer, Shelton, CT, USA), by adopting, as main reference, the [4] standard.

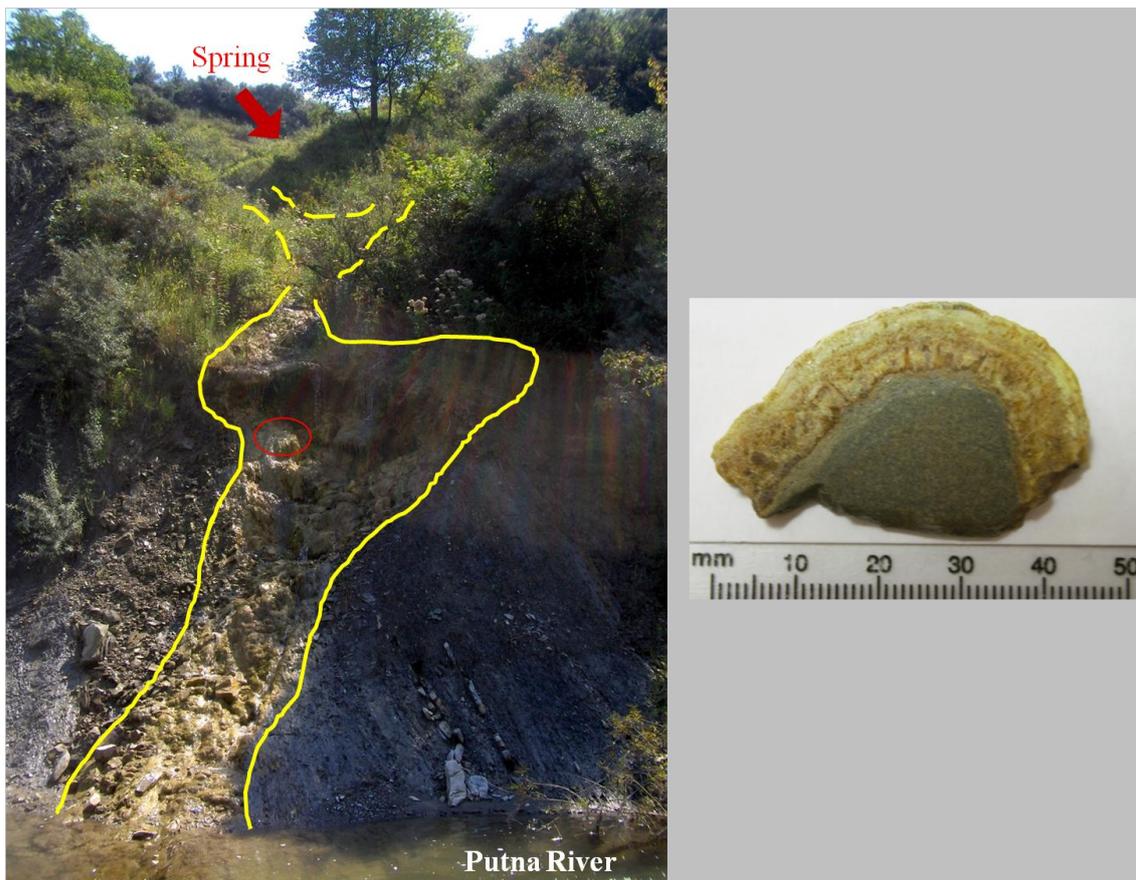


Figure 2. Photograph showing the travertine deposit (highlighted with yellow lines) precipitated along the stream (left), and detail with a travertine polished section (right). The red circle indicates the location from where the travertine sample has been collected.

For the travertine crust (Fig. 2) sample analysis, there was utilized the closed vessel microwave digestion system Multiwave 3000 Anton Paar. For analyzing the solutions resulted from the sample digestion, there was utilized the same ICP-MS equipment and procedures which were also used for the water samples.

In addition, polished sections and thin sections impregnated with dyed epoxy of the travertine samples were examined using a Steindorff NYMC-59000 trinocular polarizing microscope under transmitted light, and a CL 8200 MK3A Cold Cathodoluminescope operating at 12-15 kV and 420-430 μ A gun current.

RESULTS AND DISCUSSION

In the area where this study is focused, several cold springs emerge within a reverse fault zone, which puts in contact the Red and Grey Formations. We were interested only in one of these springs, where the calcium-bicarbonate waters caused the precipitation of a small occurrence of travertine deposited along the stream (Fig. 2). By “travertine” we refer to the term given by [5] to the freshwater carbonates formed as a result of physical and/or biological CO_2 degassing around carbonate – and CO_2 -rich springs, along the streams or pools.

The spring water samples

At all sampling dates, the spring-water temperature was virtually the same (ranging between 10.4 and 10.9°C), the pH was neutral to slightly alkaline (ranging between 7.22 and 7.93), and the TDS values were quite small (ranging between 0.36 and 0.46 g/L).

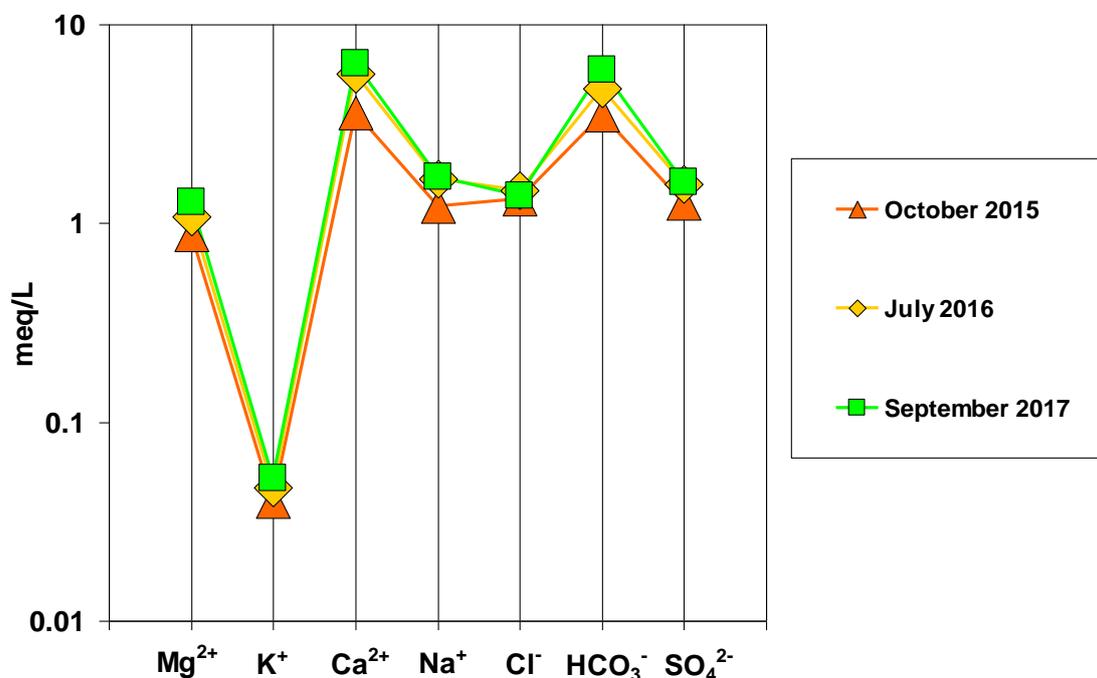


Figure 3. Modified Schoeller diagram illustrating the major constituents' concentrations in the considered spring-flow.

The chemical facies indicated by the modified Schoeller diagram (Fig. 3) was, at all sampling dates, calcium bicarbonate. This seems to indicate that meteoric-derived freshwater represented the main contribution to the total spring-flow. Still the Na^+ and Cl^- concentrations were non-negligible as well, amounting – when expressed as milliequivalents – to about one third of the HCO_3^- concentration. It was thus suggested a significant involvement of a NaCl-type water, yet the salinity possible origin – halite leaching, or fossil seawater – could not be assessed from the currently available data. On the other hand, the SO_4^{2-} anion was also abundant, its concentration – expressed as milliequivalents – amounting to about a quarter of the Ca^{2+} concentration. This instance suggested a gypsum-leaching process – which was substantiated also (see below) by the major and trace elements content of the precipitated travertine.

The travertine sample

The travertine is strongly laminated, and mainly consists of coarsely crystalline, radial-fibrous calcite crystals that often transect dark growth bands (Fig. 4A, red arrows) and bacterial shrubs, represented by clusters of peloidal micrite (Fig. 4A-B, orange arrows). In the calcite crystals there can be observed single phase aqueous inclusions which were trapped from fluids with temperatures less than 50 °C [6]. Rarely, there are found two-phase fluid inclusions which consist of water and CO_2 or CH_4 .

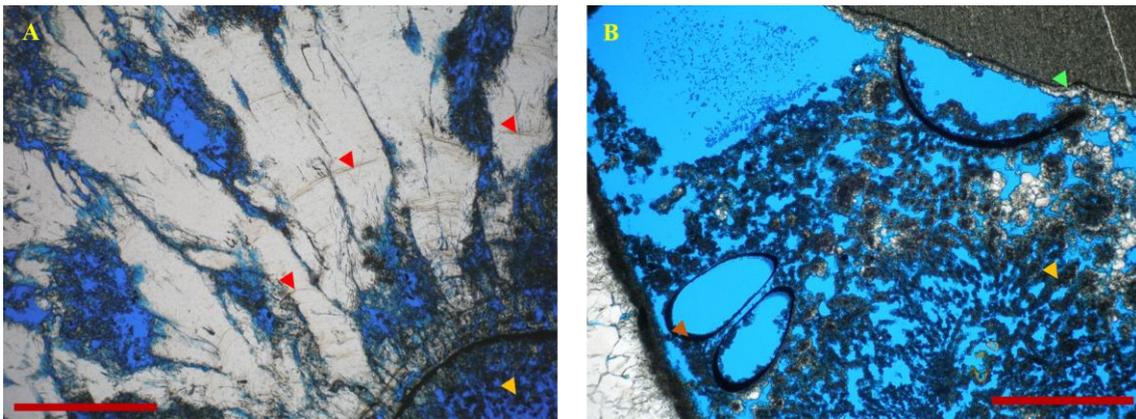


Figure 4. Thin-section photomicrographs of travertine showing different types of cement morphologies (NII, 4x). Red bar 0.5 cm. See the text for explanations.

In addition, the travertine can contain drusy, syntaxial overgrowths and isopachous calcite (Fig. 4B green arrow), which are types of cements commonly precipitated in phreatic environment, from meteoric fluids. Locally, calcitic rhombs can be observed, with more rounded edges and less regular crystal faces. According to [7], this type of calcite forms in fluids with a low salinity and a low Mg/Ca ratio, which is in agreement with our data.

Generally, the travertine has a high porosity (Fig. 4A-B blue color), with growth framework, intercrystal and moldic porosity. Also, remains of insects or plants, occasionally fossils (Fig. 4B brown arrow) like marine ostracods (probably genus *Darwinula*) can be observed. Rarely, iron oxides can be encountered as thin layers or coating the calcite crystals.

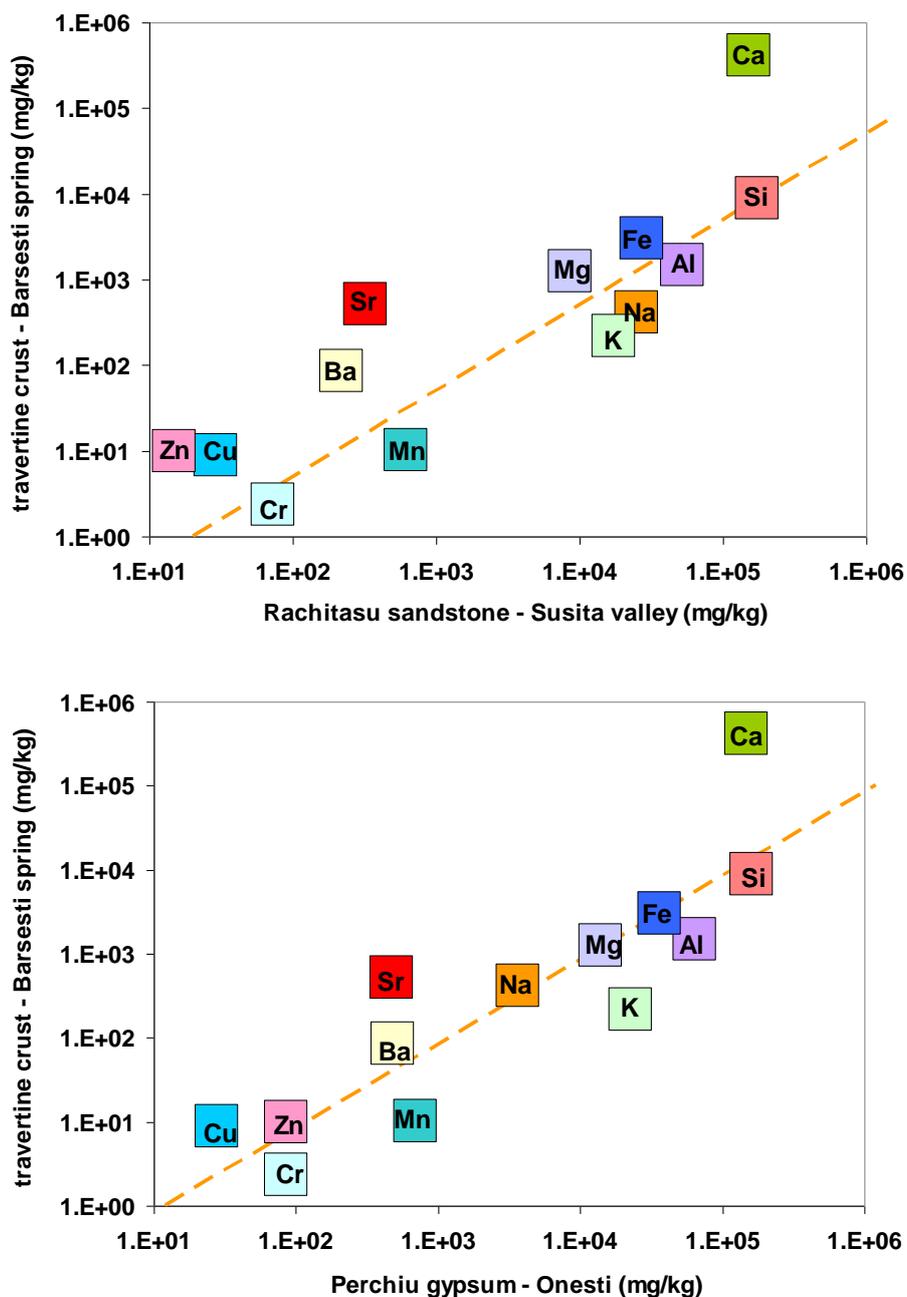


Figure 5. Concentrations of chemical constituents in the travertine crust, plotted against the concentrations of the same chemical constituents in rock formations (Rachitasu sandstone – above; Perchiu gypsum – below) which could have been leached by the discharged spring-water.

In cathodoluminescence, the travertine samples are non-luminescent, suggesting that the precipitation occurred from Fe-rich fluids.

The major and trace element concentrations of the travertine sample ranges between 1.3 to > 400 thousands ppm. The Ca content is higher than 412 thousands ppm. It is followed by Si with 8890 ppm, Fe with 3000 ppm, Al with 1470 ppm and Mg with 1240

ppm. The Sr, Na, K and Ba contents are 520 ppm, 415 ppm, 220 ppm and 85 ppm, respectively. The lowest concentrations, under 10.5 ppm are displayed by Mn, Zn, Cu, Ga, Cr and Li.

The relative content ratios between chemical elements detected in the travertine crust could be used as “fingerprints” for diagnosing which were the rocks that the spring-water had leached during its up-flow toward the ground surface. Analyses for such rock formations (specifically, for the Răchitașu sandstone and for the Perchiu gypsum formations) are provided in [8]. Figure 5 illustrates reciprocal plots – in a log-log scale – of the corresponding elements’ concentrations.

In each panel of Figure 5, a unitary slope line (dashed) was also traced: data points plotting on that line would correspond to elements which preserved in the dissolving solution exactly the same concentration ratios as those existing in the leached rock; and further on, exactly the same concentration ratios would be preserved during precipitation in the travertine deposit. In this respect, the comparison between the two panels in Fig. 5 indicates that when the Răchitașu sandstone is used as a reference, there is a broader scatter of the data points around the unitary slope line, as compared to the case when the Perchiu gypsum is used as a reference. This instance suggests that leaching of the Perchiu gypsum formation induced a stronger control on the chemical composition of the aqueous solution from which the travertine crust eventually deposited. And moreover, it is thus substantiated the inference – previously derived from the springflow abundance of sulfate – concerning the leaching of gypsum.

As normally expected, the travertine crust is strongly enriched – both with respect to the Răchitașu sandstone, and to the Perchiu gypsum – in Ca, as well as in Sr: the latter element replaces Ca, by diadochy, both in the originally leached minerals, and in the minerals deposited in the travertine crust. On the other hand, several other elements (Al, K, Mn, Cr) are depleted in the travertine as compared to the presumed leached rock: one possible cause for this fact is a lower solubility - so that smaller fractions of the concerned elements are up-taken into the aqueous solution, while at the same time, their precipitation may start earlier, before reaching the spring outlet where travertine was deposited.

CONCLUSIONS

From a cold (10.4-10.9 °C), poorly mineralized (0.36 - 0.46 g/L), and near-neutral to alkaline (pH in the 7.22-7.93 range) spring which discharges from the Subcarpathian nappe deposits, a travertine crust is precipitating. The travertine deposit is formed mainly of coarsely crystalline, radial-fibrous calcite crystals and bacterial shrubs. Calcite has precipitated into a phreatic environment from meteoric fluids with a low salinity and a low Mg/Ca ratio.

The spring-water concentrations of major and trace elements indicate that although the outflow is prevalently supplied by meteoric freshwater, there occurs as well mixing with a NaCl groundwater component, as well leaching of gypsum deposits. The latter inference is additionally supported by the fact that the chemical constituents’ ratios in the travertine crust is quite similar to the corresponding ratios in the so-called Perchiu gypsum formation, which underlies the deposits from which the spring actually

discharges. All those lines of evidence consistently suggest that the spring-water saline component originates in formations occurring at deeper levels of the Subcarpathian nappe stratigraphic sequence.

ACKNOWLEDGEMENTS

The study was partly supported by the Romanian National Authority for Scientific Research CNDI-UEFISCDI grant, project number PN-II-PT-PCCA-2011-3.1-1619 (Contract No. 48/2012).

Constructive comments and suggestions which Dr. Izabela Mariş, Dr. Marius Stoica and Gigi-Paul Dragomir provided on the considered topic are gratefully acknowledged.

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