

**MAGMA-RELATED ACID GROUNDWATERS SCAVENGE BASE-METALS
FROM THE SEDIMENTARY BASEMENT OF THE RECENTLY EXTINCT
CIOMADUL VOLCANO**

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ABSTRACT

By conducting a chemical investigation that addressed both major and trace elements dissolved in the mineral waters that discharged on the slopes of the recently extinct (ca. 27–35 ka ago) Ciomadul volcano (East Carpathians, Romania), specific processes undergone by the concerned hydrochemical system have been documented.

In terms of trace elements concentrations, it was noticed that the concentrations of Ti, V, Co, Ni and Zn never exceed several tens of ppb in near-neutral waters, while in acid waters they could reach, alternatively, several hundred ppb. Similarly, As, Cr and Pb reached up to several tens of ppb in acid waters, while in near-neutral waters their concentrations never exceeded 5 ppb. As for Cu, it was detected only in some of the acid waters, in concentrations up to almost 100 ppb.

It was next possible to refine the image suggested by this pattern, by noticing that between acid and near-neutral outlets that occurred very close (ca. 20 m) to one another, the concentration ratios were similar for most of the major components (Ca, Mg, K), as well as for some of the trace elements (Sr, Rb, Ba), being thus suggested that in both types of discharges, a common parent-water was involved. The near-neutral outlets however appeared to be strongly depleted in base-metals (Ti, V, Co, Ni, Cr, Zn, Pb) as compared to the acid fluids. The latter likely originate in the oxidation of the H₂S fraction contained in gas outflows (rich mostly in CO₂) released by a still cooling magma body: the H₂S oxidation actually occurs when those magma-derived gas outflows finally reach superficial aquifers of essentially meteoric origin.

Keywords: hydrochemical system, base-metals scavenging, acid groundwater, post-volcanic environment

INTRODUCTION

Radiocarbon dating has indicated that Ciomadul volcano had last erupted ca. 27–35 ka ago [1], being consequently the most recently extinct volcano of the East Carpathians

igneous range. The concerned volcanic edifice is underlain [2] by Early Cretaceous sedimentary deposits, which are included in two distinct units (the Convolute Flysch and the Ceahlau nappes respectively – the latter overlying the former) that belong to the East Carpathians fold and thrust belt.

That extinct volcano includes (Figure 1) a well preserved crater structure which is now hosting a lake (“St. Ana Lake”). A diffuse CO₂ flux survey conducted [3] both inside the crater and on its outer flanks indicated maximum values that only slightly exceeded those normally ascribed to biogenic processes; in contrast, diffuse CO₂ seeps measurements performed [4] about 5 km away from the crater, to the east, indicated maximum flux values which were about two orders of magnitude higher. Such a circumstance is consistent with a previous observation of [5], who had noticed that the mantle fluids contribution (as indicated by ³He/⁴He ratios in dry gas exhalations and in mineral water discharges) was significantly smaller close to the crater than several kilometers to the east. It is hence obvious that this gas and mineral water discharge region situated east of the Ciomadu crater, and included in the present-day Balvanyos resort, is of utmost interest for elucidating the pattern of post-volcanic fluids release pathways.

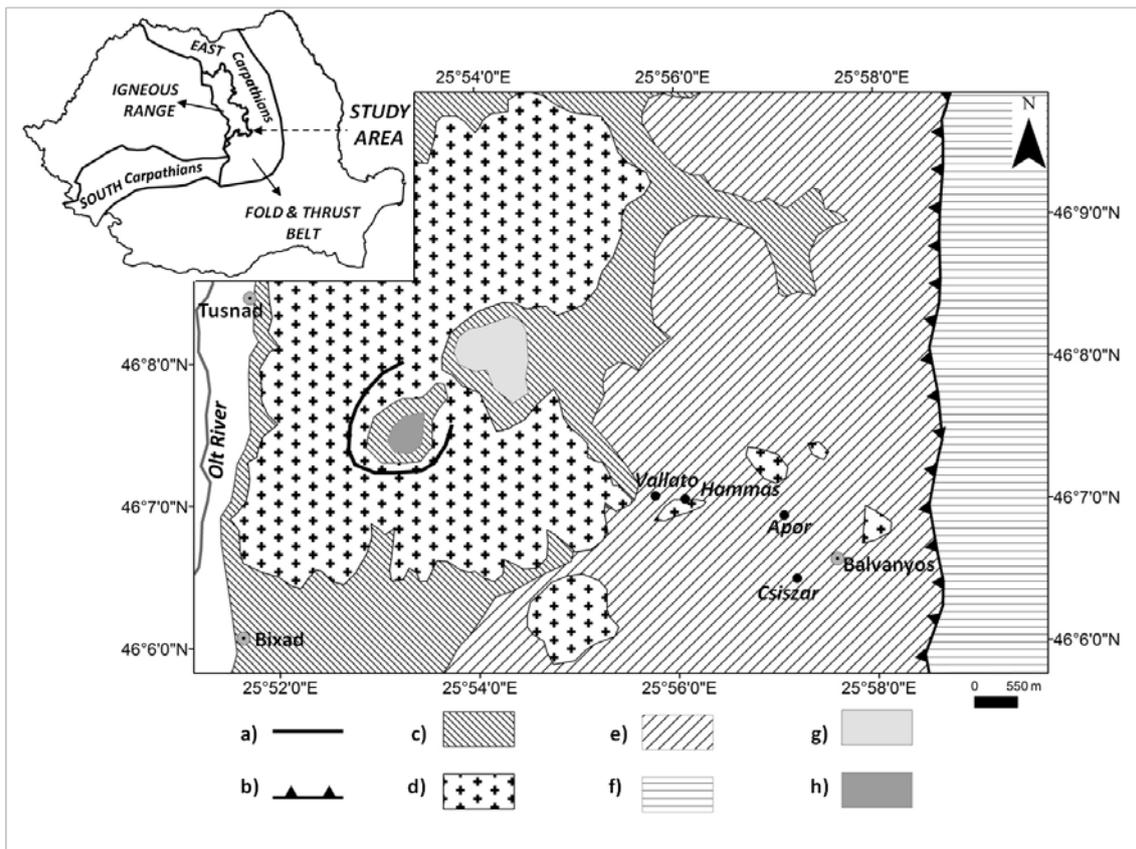


Figure 1 - Location map of the concerned clusters of mineral water outflows (geology after [9]): a) St. Ana crater rim; b) Overthrust; c) Volcaniclastic deposits; d) Dacite (domes and lava flows); e) Cretaceous flysch of the Ceahlau nappe; f) Cretaceous flysch of the Convolute nappe; g) Mohoš peat bog deposits; h) St. Ana lake. The index map illustrates the study area location on the territory of Romania

SAMPLING AND ANALYTICAL APPROACH

The area surrounding the volcano edifice hosts a multitude of mineral groundwater discharges which might provide significant information on the current status of the still active inflows of magma-derived fluids. Most of the possibly relevant hydrogeological and hydrochemical information published about those groundwater outlets is, however, several decades old [6]. A recent (2015) survey has therefore been conducted, and it outlined that mineral water outflows usually occurred as clusters (locally designated as “spas” – e.g., Apor, Csiszar, Hammas, Vallato - Figure 1), which were located, on the average, about 1 km away from each other. A remarkable feature is that within each specific cluster, some discharges are acid (pH from 1.35 to 4.1), while others have near-neutral pH (in the range 5.5 to 6.5); yet their chemical type is, in most cases, the same – namely CaSO₄. The distances that separate, from one another, such nearby outlets of contrasting acidity range from a few meters to a few tens of meters.

Groundwater samples were collected in Nalgene High-Density Polyethylene bottles. When collected, the samples have been filtered by using Thermo Scientific Chromacol Polyether Sulphone Syringe Filters (0.45 µm pore size). Suprapur (Merck) 65% nitric acid was used for the pH adjustment of the collected samples.

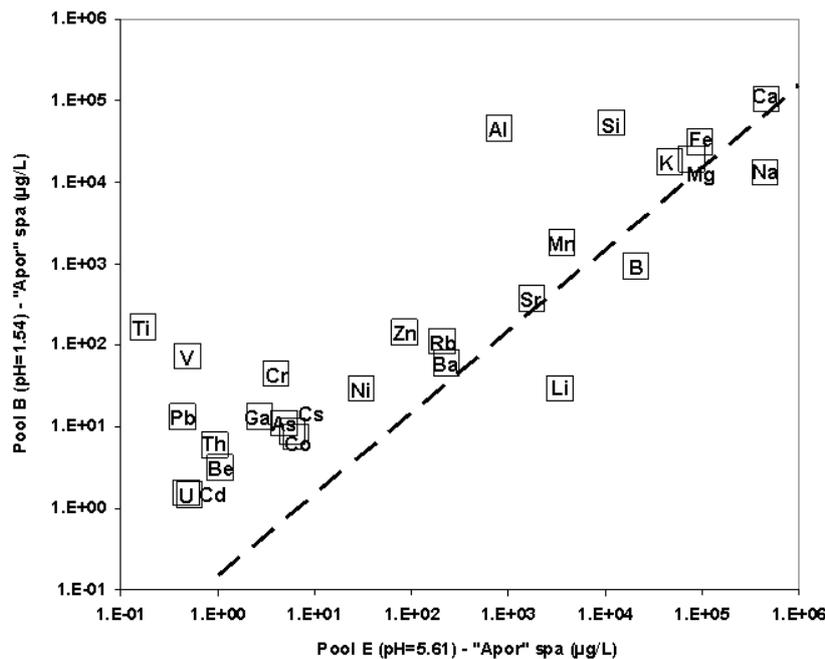


Figure 2 - Log-log reciprocal plot between the solutes' concentrations determined in the outlets B (pH=1.54) and E (pH=5.61) of "Apor" spa. For reference, a unitary slope line (dashed) is indicated.

The complete chemical analysis of all collected water samples was conducted in the Hydrogeochemistry Laboratory of the “Emil Racoviță” Institute of Speleology. The concentrations of all components considered by the present paper have been determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), specifically: Li, Be, B, Tl, Si, Pb, Th, U, Cl and Br in the standard mode; Na, K, Rb, Cs, Mg, Sr, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Al, Ga and As by the collision mode with Kinetic Energy

Discrimination (KED-ICP-MS); while Ca and Ba by means of the Dynamic Reaction Chamber (DRC-ICP-MS) technique. All determinations were conducted in compliance with the US-EPA 6020B standard [7]. The measurements were carried out with a NexION 300S (PerkinElmer, Shelton, CT, USA) ICP-MS instrument, equipped with a S10 Autosampler.

RESULTS AND DISCUSSION

A preliminary observation was that in near-neutral waters, the concentrations of Ti, V, Co, Ni and Zn never exceed several tens of ppb, while they could reach, alternatively, several hundred ppb in acid waters. Similarly, As, Cr and Pb reached up to several tens of ppb in acid waters, while in near-neutral waters their concentrations never exceeded 5 ppb. As for Cu, it was detected only in some of the acid waters, in concentrations up to almost 100 ppb.

The image suggested by this pattern was additionally refined by constructing, both for the major, and for the trace elements, reciprocal concentrations plots (Figures 2-5). One such plot (Figure 2) was used for making a comparison between the compositions of the mineral water outlets B (pH=1.54), and E (pH=5.61), which were located just 20 m away from each other, within the so-called "Apor spa" (Figure 1).

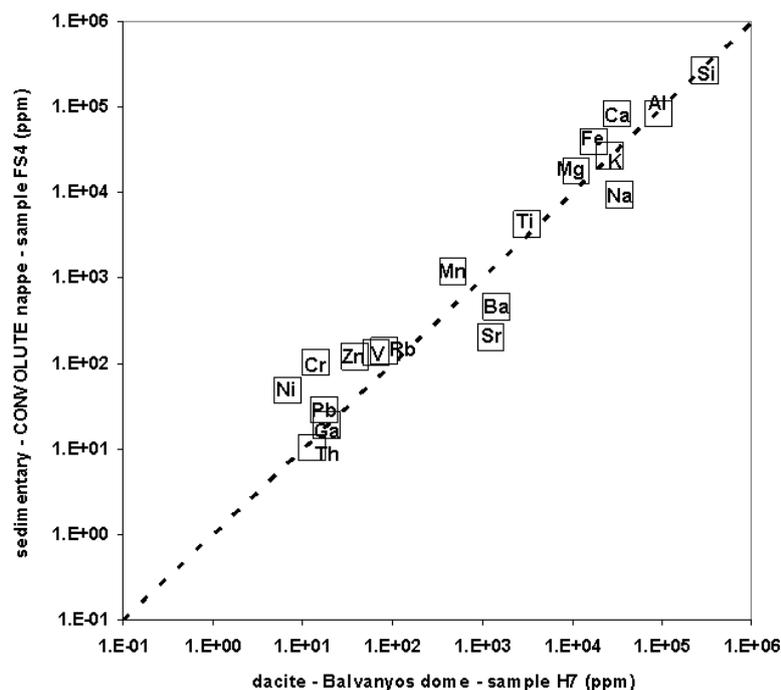


Figure 3 - Log-log reciprocal plot between elements' concentrations determined for the sedimentary and igneous rocks (raw data from [2]) that could possibly host the mineral water flows. An equal concentration line (dotted) is indicated for reference.

With reference to a "unitary slope line" (that corresponds to dilution of a mineralized water by zero-concentration freshwater), it appears that a rough correlation exists between the corresponding alkaline and alkaline earth metals concentrations, being accordingly suggested that a common parent-water was involved in both types of

discharges - with the acid outlet still being more diluted. That acid outlet (pool B) is, on the other hand, significantly enriched in base-metals (Ti, V, Pb, Cr, Cd, Co, Ni, Zn) and in As, as compared to the near-neutral outlet. One possible explanation for this distinction between near-neutral and acid groundwaters could be water-interaction with different rock-types.

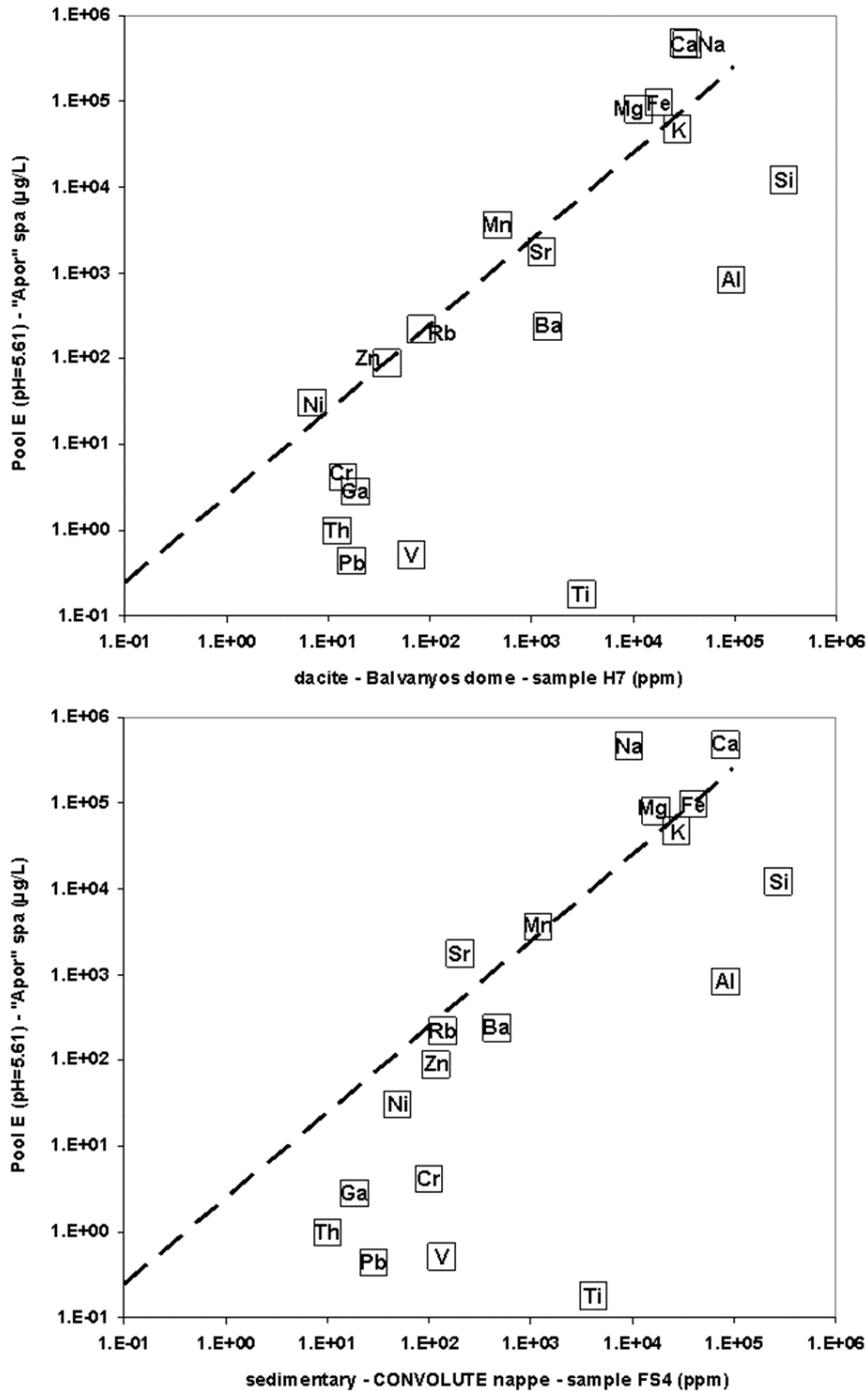


Figure 4 - Log–log plot of the "Apor spa" pool E (pH=5.61) major and trace elements' concentrations, vs. the compositions of corresponding possible host-rocks, of either igneous or sedimentary nature. For reference, a unitary slope line (dashed) is indicated.

Geological formations with which mineral waters sampled at “Apor” spa could possibly interact are (i) dacite (belonging to one of the Ciomadul volcano peripheral domes); (ii) Early Cretaceous flysch deposits included in one of the two previously mentioned - “Convolute” and “Ceahlau” - nappes.

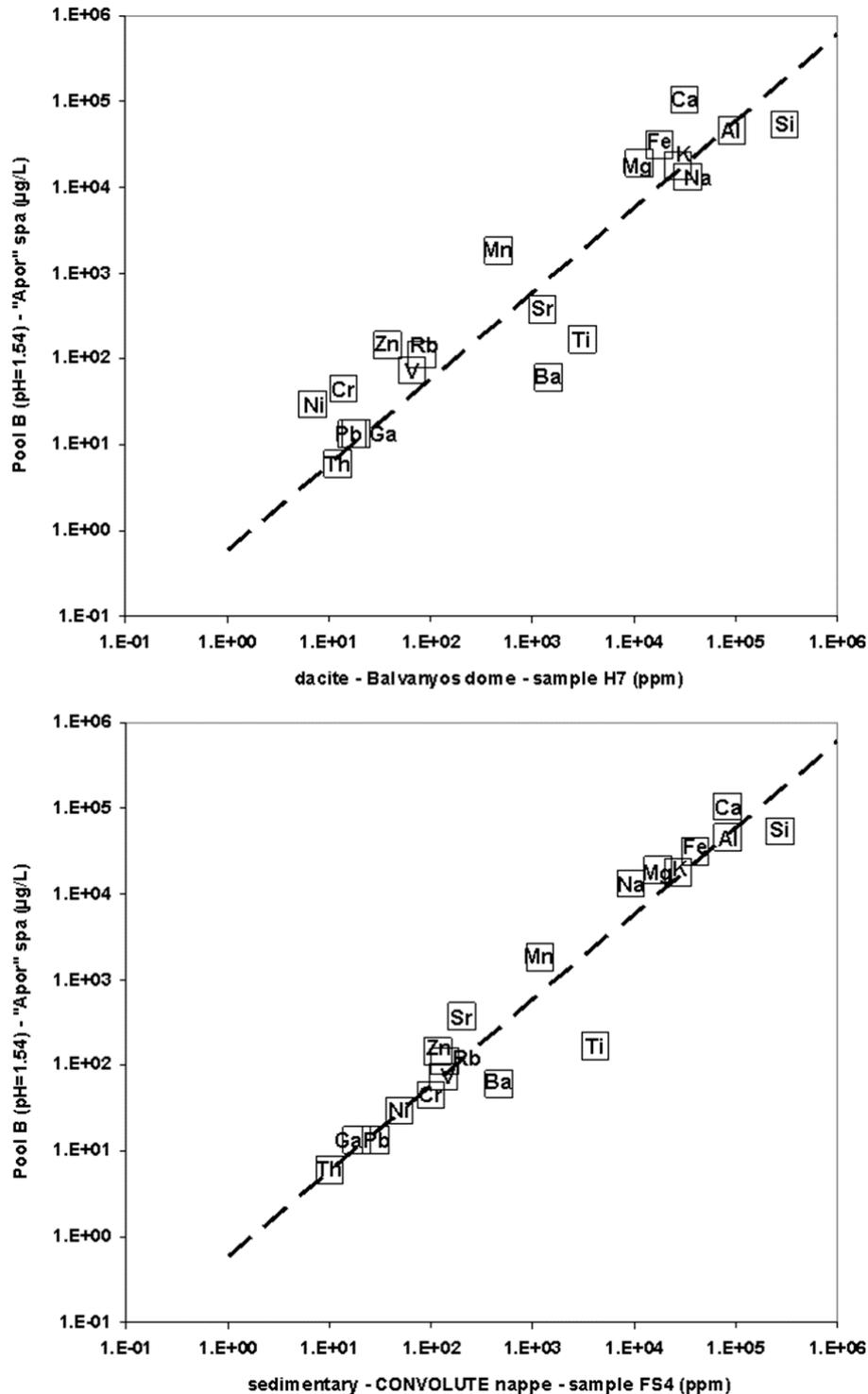


Figure 5 - Log-log plot of the “Apor spa” pool B (pH=1.54) major and trace elements’ concentrations, vs. the compositions of corresponding possible host-rocks, of either igneous or sedimentary nature. For reference, a unitary slope line (dashed) is indicated.

Major and trace constituents' concentration values for corresponding rock samples have been provided in [2]. Accordingly, as illustrated by Figure 3, igneous rocks (dacite) appear to be, by comparison with sedimentary formations (in particular, those of the Convolute nappe) enriched in Sr and depleted in certain base metals (Ni, Cr, Zn). While at the same time, sedimentary formations belonging to the two flysch nappes (not shown) display chemical compositions that are very similar to one another.

Next, by comparing the pool E (near-neutral pH water) chemical composition with that of the rock formations with which it could possibly interact, a reasonable similarity was noticed (Figure 4) only with igneous rocks (dacite), while correlation with the Cretaceous sedimentary series of the volcano basement appeared to be much poorer.

In contrast, when the acid water (pool B) chemical composition is compared (Figure 5) to that of the rock formations with which it could possibly interact, the correlation with igneous rocks appears to be much poorer, in comparison with the good similarity noticed with the Cretaceous sedimentary series (in particular, those of the Convolute nappe). Consequently, if one takes in to account the sedimentary deposits base metals enrichment with respect to dacite (Figure 3), corroborated with the acid fluids base metals enrichment with respect to near-neutral pH fluids (Figure 2), the hypothesis of base-metals being scavenged, by the acid fluids, from the Convolute nappe flysch formations appears to be strongly supported.

The concerned acid groundwaters likely originate in the oxidation of the H₂S fraction contained in gas outflows (rich mostly in CO₂) released (e.g., [8]) by a still cooling magma body; the H₂S oxidation actually occurs when those magma-derived gas outflows finally reach superficial aquifers of essentially meteoric origin.

CONCLUSION

In spite of occurring very close (cca. 20 m) to one another, the “B” and “E” groundwater discharges of “Apor” spa are dissimilar - both in terms of pH values (highly acid, versus near-neutral respectively), and in terms of their chemical constituents concentrations.

A rough correlation between the corresponding alkaline and earth-alkaline cations seems to suggest that a common parent-water could be involved in both types of discharges, with the acid outlet being more diluted by freshwater. The concerned acid groundwater likely originates in the oxidation of the H₂S gas outflows that are released by a still cooling magma body; H₂S oxidation actually occurs when those gas outflows reach superficial aquifers of essentially meteoric origin.

On the other hand, as compared to the near-neutral spring water, the acid outlet is significantly enriched in base-metals (Ti, V, Pb, Cr, Cd, Co, Ni, Zn) and As.

With respect to the composition of the rocks with which they could possibly interact, the near-neutral spring water displayed a rough similarity with the dacite, while the acid water mimicked very well the composition of a Convolute nappe rock-sample.

Given that as compared to the dacite, the flysch formations of the nappes are significantly enriched in base metals, it appears that overall considered, acid fluids

scavenge such base-metals from the sedimentary formations which underlie the volcano edifice.

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REFERENCES

- [1] Szakács A., Seghedi I., Pécskay Z., Mirea V., Eruptive history of a low-frequency and low-output rate Pleistocene volcano, Ciomadul, South Harghita Mts., Romania, *Bulletin of Volcanology*, vol. 77/issue 2, pp 1-19, 2015.
- [2] Mason P.R.D., Downes H., Thirlwall M.F., Seghedi I., Szakács A., Lowry D., Matthey D., Crustal assimilation as a major petrogenetic process in the East Carpathian Neogene and Quaternary continental margin arc, Romania, *Journal of Petrology*, U.K., vol. 37/issue 4, pp 927-959, 1996.
- [3] Frunzeti N., Baciuc C., Diffuse CO₂ emission at Sfânta Ana lake-filled crater (Eastern Carpathians, Romania), *Procedia Environmental Sciences*, vol. 14, pp 188 – 194, 2012.
- [4] Papp B., Szakács A., Néda T., Frunzeti N., Szacsvai K., Cosma C., Soil radon and thoron activity concentrations and CO₂ flux measurements in the Neogene volcanic region of the Eastern Carpathians (Romania), *Carpathian Journal of Earth and Environmental Sciences*, Romania, vol. 9/issue 1, pp 261-268, 2014.
- [5] Althaus T., Niedermann S., Erzinger J., Noble gas studies of fluids and gas exhalations in the East Carpathians, Romania, *Chemie der Erde - Geochemistry*, Germany, vol. 60/issue 3, pp 189-207, 2000.
- [6] Bandrabur T., Slăvoacă D., Ianc R., Utilization prospects for the mineral waters in the Balványoş-Turia-Iaidon area, *Studii Tehnice și Economice*, Institutul de Geologie și Geofizică București, Romania, Seria E, vol. 14, pp 41-61, 1984 (in Romanian).
- [7] US-EPA - Method 6020B. Inductively Coupled - Mass Spectrometry. Revision 2, July 2014.
- [8] Mitrofan H., Tuşnad-Băi - a geothermal system associated to the most recent volcanic eruption in Romania, *Proceedings of the World Geothermal Congress*, Japan, 2000, pp 1447-1452.
- [9] Săndulescu M., Vasilescu A., Popescu A., Mureşan M., Arghir-Drăgulescu A., Bandrabur T., *Geological Map of Romania*, scale 1:200,000, Odorhei sheet, Institutul Geologic, Bucureşti, Romania, 1966.