

TRACE ELEMENTS GEOCHEMISTRY INVESTIGATION CONCERNING A CO₂-RICH GROUNDWATER DISCHARGE ON THE EASTERN FLANK OF CIOMADUL VOLCANO (EAST CARPATIANS, ROMANIA)

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ABSTRACT

Ciomadul volcano is the site of the youngest eruptive activity (1.0 and ≤ 0.1 Ma) from the Carpathian areas and it has developed on a folded basement consisting of flysch series of the East Carpathians. In the areas surrounding Ciomadul volcano there occur abundant discharges of CO₂-rich groundwater, both from natural springs and from drilled wells. One such well, located on the eastern flank of Ciomadul volcano has crossed the Lower Cretaceous flysch deposits of the Ceahlău Nappe down to 1203 m depth, where it has stopped in pyroxene-bearing andesite. The well supplies a CO₂ - water mixture from which a calcite-iron oxides crust has resulted. Both water and crust samples were collected and chemically investigated for assessing the precipitating fluids origin. Water samples exhibit major elements concentrations considerably lower than the ones displayed by the crust samples. It seems that the fluids responsible for the precipitation of the calcite-iron crust are most likely of mixed-meteoric and volcanic origins.

Keywords: trace elements, fluids, post-volcanic activity, East Carpathians.

INTRODUCTION

The southern part of Harghita Mountains has been extensively studied, the addressed topics focusing on volcanism [1, 2], geophysics [3, 4], water chemistry and gas emissions [5, 6], etc. In this paper, based on a chemical investigation, a first attempt is made to determine the origin of groundwater by studying the minerals precipitated in the form of calcite-iron oxides crusts.

The analyses were carried out in Bálványos area, located on the eastern flank of Ciomadul volcano, Harghita Mountains. The studied well (Fig. 1A) has crossed the marine sedimentary sequence of the Ceahlău Nappe down to 1203 m depth, where it has stopped in pyroxene-bearing andesite. The presently completed interval (175-240 m depth) supplies a CO₂ - water mixture that is intermittently discharged every few hours resulting in the precipitation of a calcite-iron oxides crust (Fig. 1B), formed by alternating thin layers of calcite and iron-oxides, most probably hematite.

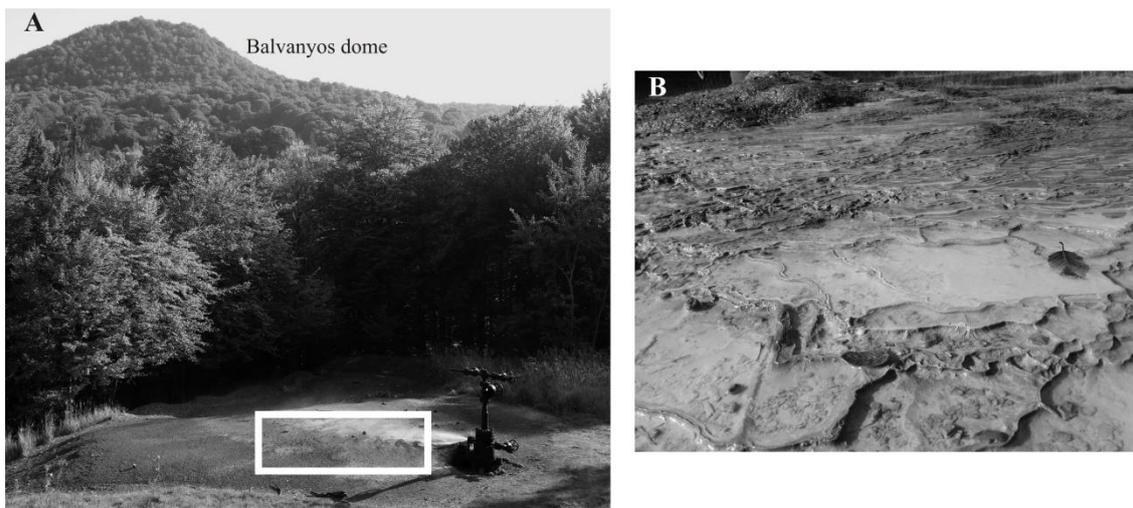


Figure 1. Photographs showing the discharging well located on the eastern flank of Ciomadul volcano (A), and detail on the calcite-iron oxides crust resulted from the water discharges.

GEOLOGIC SETTING

Ciomadul volcano is developed over an area of 80 km² [1] in the most southern part of Harghita Mountains, right on the border between the Transylvanian Basin and the East Carpathians (Fig. 2, inset). It represents a dacitic dome complex built on top of folded and thrustured Lower Cretaceous flysch deposits belonging to the Ceahlău nappe. The volcanic structure, with ages between 1.0 and ≤ 0.1 Ma [1], is dominated by a central group of extrusive domes surrounded by few isolated peripheral domes (Fig. 2).

The Ceahlău nappe consists of a Tithonic-Neocomian sericite schists sequence, followed by a Barremian-Albian flysch sequence built up of calcareous deposits and then, alternating marls and sandstones deposits [7].

SAMPLING AND ANALYTICAL APPROACH

The water samples were collected from a well located in Bálványos area. Water discharged by the well has been sampled, once every 1-2 months, between June 2008 and May 2010. During summer of 2015, the calcite-iron oxides crust was sampled every 2 m along a 20 m profile striking NNE away from the well.

The complete chemical analysis of all crust and water samples was conducted in the Hydrogeochemistry Laboratory of the “Emil Racoviță” Institute of Speleology of the Romanian Academy. In the following, there are essentially indicated only the techniques utilized for analyzing the components addressed by the present paper.

The closed vessel microwave digestion system (Multiwave 3000, Anton Paar) was used to digest the calcite-iron oxides crust samples and placed in Teflon digestion vessels with 4 mL HCl, 2 mL HF, 2 mL HNO₃ (all Suprapur, Merck) and 2 mL ultrapure water. The digestion program was: power, 1400 W; ramp time, 10 min; hold time, 35 min and cooling time, 30 min. After digestion, sample solutions were transferred quantitatively into 50 mL volumetric flasks and made up to 50 mL with ultrapure water (LaboStar TWF UV7 Ultrapure Water System, electric resistance 18.2M Ω ×cm). A blank digest was carried out in the same way.

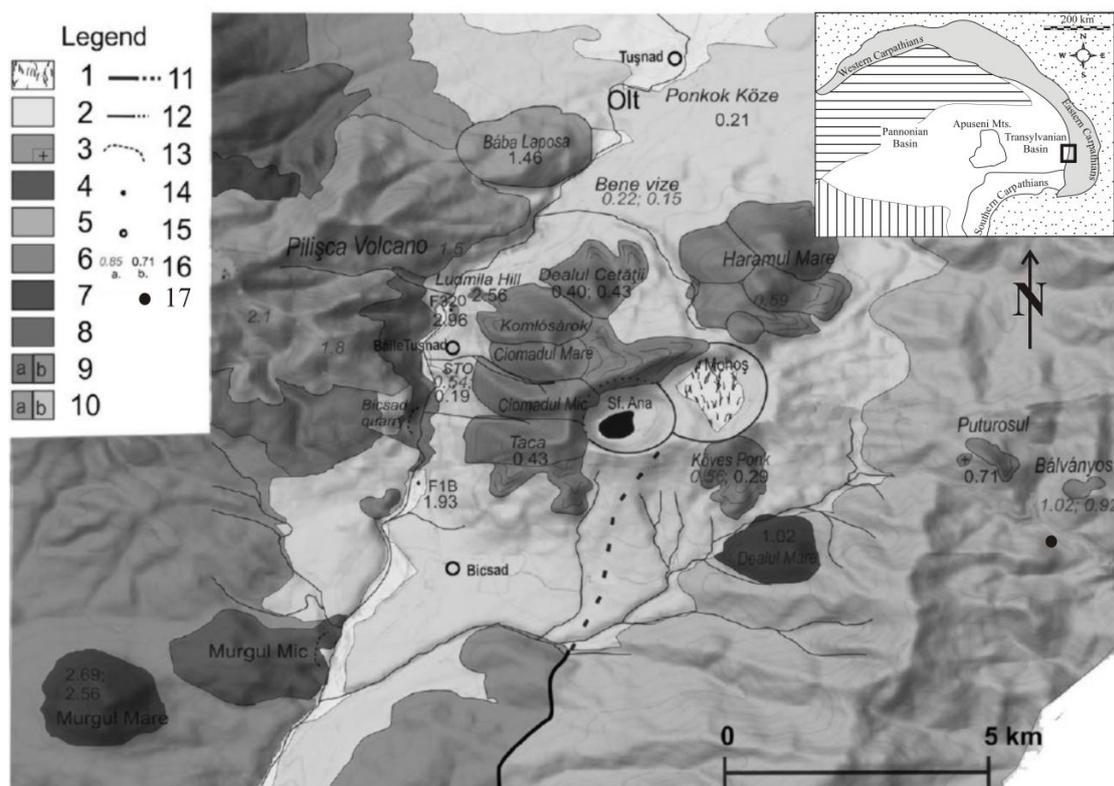


Figure 2. Geological map of Ciomadul volcano (after [1]). Simplified Legend: 1. Mohoş swamp; 2. Ciomadul volcano-volcanoclastic deposits; 3. Ciomadul dacite domes, "+" intrusion; 4. Dealul Mare andesite dome; Pilişca volcano: 5. andesite and dacite domes, 6. andesite with Am and Px, and 7. basaltic andesite; 8. Shoshonite (Murgul Mic dome); 9. Cucu volcano: a. Andesite, b. Volcaniclastic deposits; 10. Cretaceous flysch deposits: a. Tithonic-Neocomian, b. Barremian-Albian; 11. Fault; 12. Crater outline; 13. Quarry; 14. Drilling; 15. Town; 16. K-Ar age; 17. Well. Inset shows the location of Harghita Mountains within the Carpathian-Pannonian region.

The solutions resulted from samples digestion and water samples were analyzed by means of standard inductively coupled plasma mass spectrometry method [8]. The determinations were carried out with a NexION 300S (PerkinElmer, Shelton, CT, USA) ICP-MS instrument, equipped with a S10 Autosampler. The instrument was set to work in Kinetic Energy Discrimination (KED-ICP-MS) mode or Dynamic Reaction Chamber – technique (DRC-ICP-MS).

RESULTS AND DISCUSSION

Major differences regarding the major elements content can be observed between the water and calcite-iron oxides crust samples.

In water samples, the K and Ca concentrations never exceeded a few hundred ppm, 570 to 600 ppm for K and 400 to 900 ppm for Ca, respectively. Instead, Mg displayed concentrations around 90 to 98 ppm, and Si concentrations below 17 ppm. As for Na, its concentration never fell below 10 thousand ppm.

By contrast, the concentrations of Ca and Si from the calcite - iron oxides crust proved to be much higher, the values significantly decreasing as one moves away from the well. The corresponding concentrations can reach up to 250 thousand ppm for Ca and 35 thousand ppm for Si. The Na content is slightly decreased and ranges between 5000 to 9000 ppm. In case of K and Mg, the concentrations rarely exceed a couple of thousands ppm, 570 to 1850 ppm to K and 1680 to 4700 ppm for Mg, respectively.

The crust samples also display noticeable concentrations of Ba, Sr and Al. The values range between 1850 to 9500 ppm for Ba, 1500 to 3050 ppm for Al and 2100-2800 ppm for Sr, respectively. In addition, small amounts (up to 225 ppm) of Ga and Li, and trace amounts (under 35 ppm) of Zn, Cr and Cu, were observed.

A reciprocal concentrations plot was constructed for the major and trace elements determined in the two samples collected from the bottom, and from the top respectively of the crust deposited around the wellhead (Fig. 3). While most elements seem to be present, in those two samples, in comparable concentrations, it still appears that the top sample is significantly enriched in Ca, in some base metals (Cu, Cr), and in Al. One possible explanation could reside in the fact that each sample was deposited by water having interacted with different rock-types.

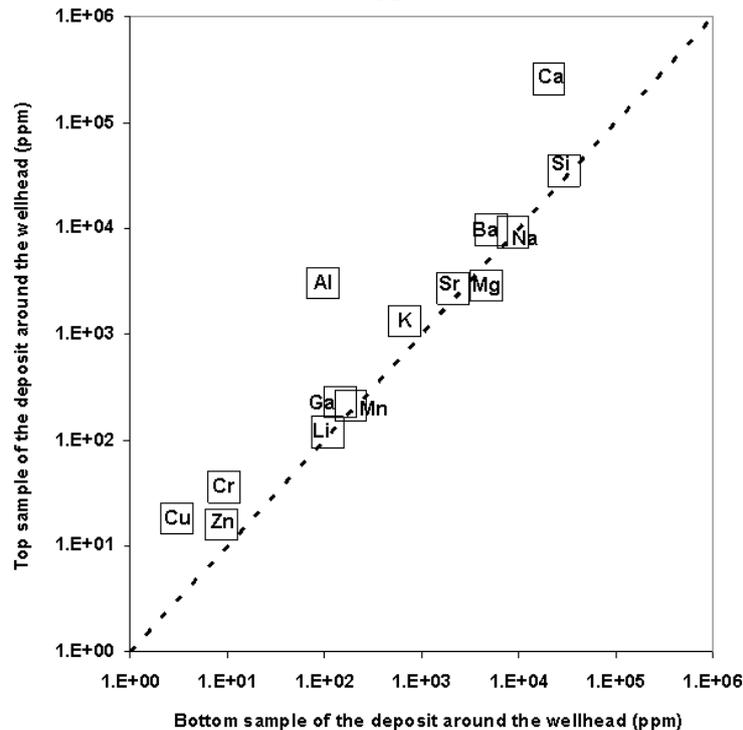


Figure 3. Log-log reciprocal plot between the major and trace elements' concentrations determined in the samples collected from the bottom and the top of the deposit around the wellhead. An equal concentration line (dotted) is indicated for reference.

Geological formations with which the water discharged by the well could have possibly interacted are (i) andesite (possibly dacite) intercepted at the well bottom and involved in the first discharge test; (ii) Early Cretaceous flysch deposits tapped during subsequent discharge tests.

Major and trace constituents' concentration values for corresponding rock samples have been provided in [2].

By comparing the chemical composition of the bottom sample of the deposit around the wellhead, with the compositions of the indicated possible aquifer rocks, a reasonable similarity was noticed (Fig. 4 left column) only with igneous formations (dacite), while correlation with the Cretaceous sedimentary series of the volcano basement appeared to be much poorer.

In contrast, when the chemical composition of the top sample of the deposit around the wellhead is compared (Fig. 4 right column) to that of the possible aquifer rocks, the correlation with igneous formations appears to be much poorer, in comparison with the good similarity noticed with the Cretaceous sedimentary series of the Ceahlău nappe.

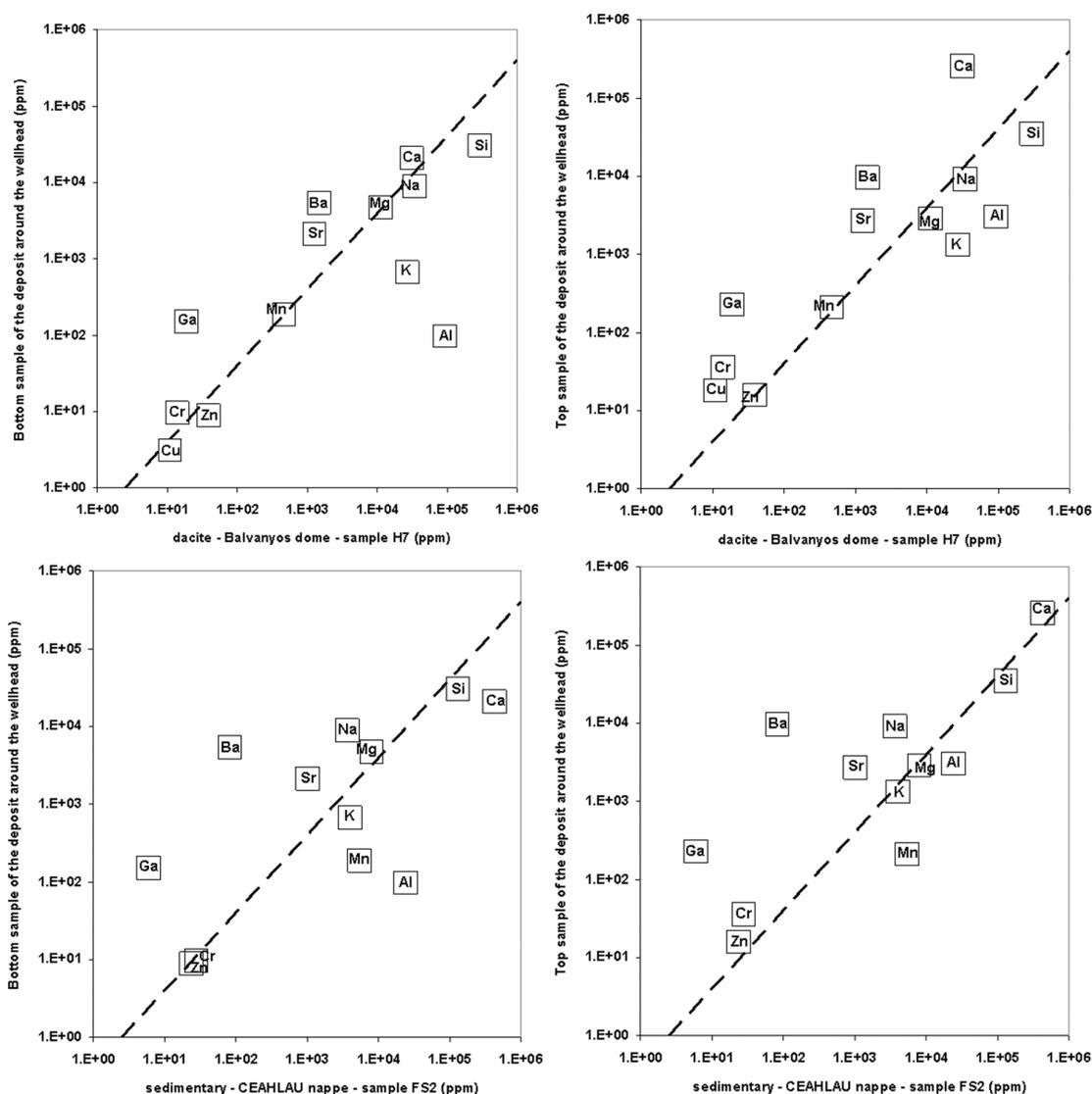


Figure 4. Log–log plot of major and trace elements' concentrations in the bottom (left column) and top (right column) samples of the deposit around the wellhead, vs. the compositions of possible aquifer rocks, of either igneous or sedimentary nature. For reference, a unitary slope line (dashed) is indicated.

Although, the bottom sample shows similarities with the igneous rocks, while the top samples are more resembling with the sedimentary rocks, we can assume that the fluids responsible for the calcite-iron oxides crust formation are most likely of mixed - meteoric and volcanic - origins. On the one hand, the meteoric fluids were enriched in Ca, Mn, Fe, Zn, Li and Al as a result of the interaction with the sedimentary marine deposits, most probably from the Ceahlău Nappe. On the other hand, the volcanic fluids are enriched in Sr, Ba, Cr and Ga, being also accompanied by CO₂ emissions.

CONCLUSIONS

This work represents the first survey that tries to investigate the origin of CO₂-rich groundwater by studying the products of their discharges. The CO₂-rich groundwater discharges was provided by a well located on the eastern flank of the Ciomadul volcano. The outcome of these discharges consisted in the calcite-iron oxides crust formation.

The major and trace elements investigation carried out on both water and calcite-iron oxides samples revealed that: (i) the water discharges display major elements content considerably lower than the calcite-iron oxides crust; (ii) the differences in the trace elements concentrations registered around the wellhead could have originated from the water interaction with different rock-types, igneous rocks at the bottom and sedimentary rocks at the top, respectively; (iii) the calcite-iron oxides crust along the profile display trace elements concentrations that could have originated from the interaction between water and the sedimentary rocks.

Although the calcite-iron crust exhibits similarities with both igneous and sedimentary rocks, the groundwater enriched in CO₂ were most likely of mixed meteoric-volcanic origin.

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