POSTVOLCANIC PROCESSES SUGGESTED BY THE MINOR AND TRACE ELEMENTS CONTENT OF COLD FRESHWATER BODIES LOCATED WITHIN THE CIOMADUL QUATERNARY VOLCANO

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According to previous investigations, Ciomadul volcano, in the East Carpathians, has discontinuously erupted between about 1 Ma and 30 ka ago. Despite the relatively long duration of the current dormancy period, the volcanic magma reservoir could still be partly molten, as suggested by nearby outflows of magmatic gases and thermo-mineral water. But such fluid discharges have so far been detected just on the lower slopes of the volcanic edifice: in contrast, the only two obvious crater structures, St. Ana and Mohoş, are presently occupied by cold freshwater lakes. An aquifer saturated with fresh and cold groundwater was identified as well, by means of a domestic well dug on the ridge separating the craters. By analyzing the contents of minor and trace elements (Ba, Sr, Rb, Li, V, Cr, Mn, Co, Ni, Cu, Zn, Cd, Ga, As) of the two lakes and of the nearby groundwater body, we attempted to acquire information on the hydrochemical processes which operated within the corresponding upper segment of the volcanic edifice. Overall considered, both lakes as well as the groundwater display rather similar signatures in terms of minor and trace elements, most probably ensuing to the dissolution of a common substratum of igneous rocks. Anomalous behaviors were however noticed in the case of strontium (Sr) and lithium (Li). The water of both lakes is significantly depleted in Sr as compared to the groundwater, possibly because of the intense alteration undergone in the past by the lake bottom deposits, resulting in advanced removal of that relatively mobile element. The Li concentrations in Mohoş lake and in the groundwater are very similar with each other, but far larger (by almost two orders of magnitude) than the corresponding concentration of St. Ana lake. This circumstance could indicate – given that Li is very mobile and likely present in magmatic gas – that "concealed" inputs of such volatiles still occur in the proximity of Mohoş crater (where also the domestic well intercepting the aquifer is located), in contrast, St. Ana crater receives no similar gas inflows, and neither seems to be its lake connected to the aquifer identified on the ridge separating the two craters.

Keywords: Trace, Elements, Ciomadu, Volcano.

1. GEODYNAMIC AND HYDROGEOLOGICAL SETTING

The most recent eruption having been outlined so far within the eastern Carpathians volcanic chain is the one associated to Ciomadul volcano. The corresponding event has been dated both by means of radiocarbon, and by means of the zircon minerals contents of U-Th and (U-Th)/He, being accordingly established (Harangi *et al.*, 2015) that it had taken place about 32 ky BP. Despite such a long period of inactivity, two well preserved crater structures are still visible within Ciomadul volcano (Fig. 1). The most typical morphology is displayed by the crater which is nowadays hosting St. Ana Lake. The second crater, whose morphology is not so well-defined, is hosting a peat bog named Mohoş.

A survey of the CO_2 diffuse emissions has been conducted both in the interior of St. Ana crater, and over its outer slopes (Frunzeti & Baciu, 2012): the accordingly recorded maximum gas fluxes only slightly exceeded values that were normally associated with biogenic processes. Yet CO_2 diffuse emissions recorded by Papp *et al.* (2014) some 5 km E of St. Ana crater have outlined maximum gas fluxes that were much larger (by about two orders of magnitude). Such a setting is consistent with previous results of Althaus *et al.* (2000):

based on $^{3}He/^{4}He$ ratios measured in dry gas vents and in mineral water occurrences, they had established that mantle-derived fluids contribution close to St. Ana Lake was considerably lower as compared to inputs occurring several kilometers to the east.

It was accordingly suggested that post-volcanic fluids upflow pathways could be associated with the gas vents and mineral water occurrences situated east of St. Ana Lake. At the same time, the multitude of mineral water outflows existing on the outer slopes of Ciomadul volcano are a favorable pre-requisite for attempting to diagnose fluid flows regime possibly associated with degassing of a still partially molten lava body. Yet currently, the groundwater accumulations distribution within Ciomadul volcano is poorly known.

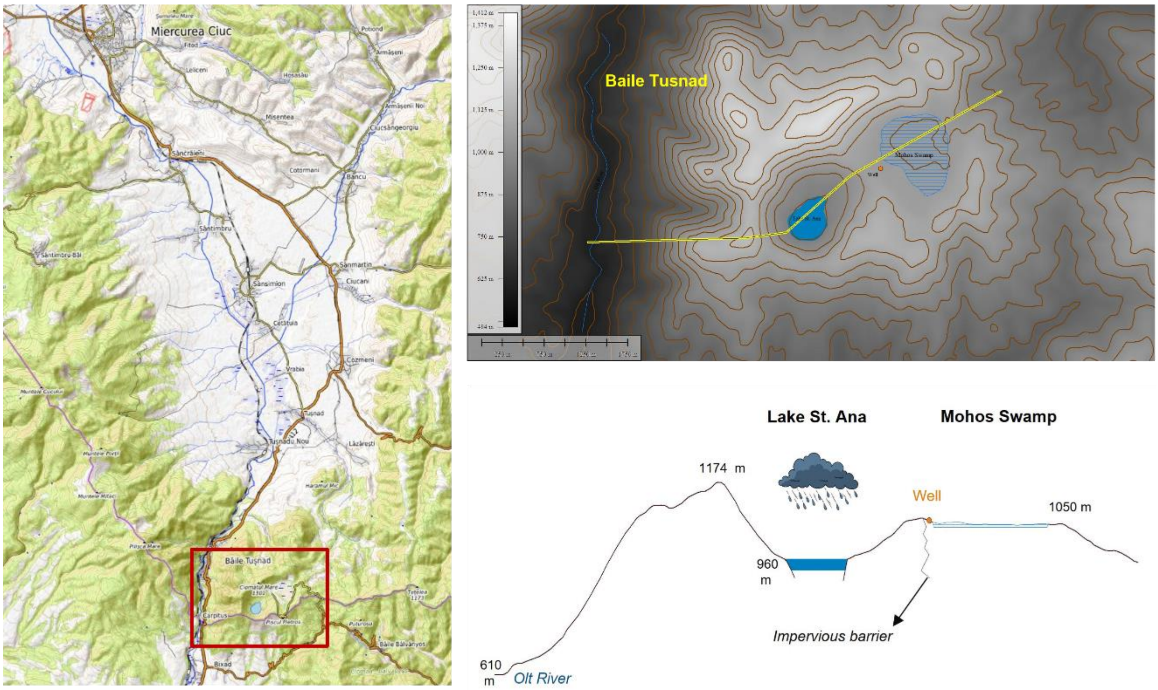

Figure 1 – Morpho-hydrogeological sketch in the area of St. Ana and Mohoş crater lakes. A. Plane view. B. Cross section along the profile indicated in image A. C. Location of the study area (rectangle).

The aquifer positioned at the highest altitude has been intercepted by a domestic water well situated at 1060 m a.s.l., on the western rim of Mohoş crater, close to the wind gap which separates the latter from St. Ana crater (Fig. 1). In that well, the water level is situated some 10 m higher than the water surface of Mohoş peat bog: it therefore seems probable that the phreatic aquifer intercepted by the well is recharging Mohoş peat bog; the latter next supplies - via an erosional breach in the rim of the former crater – the flow of Veress surface stream.

In contrast to Mohoş crater, the adjoining St. Ana crater is entirely closed, and its hydrogeological setting is more difficult to be assessed. The previously mentioned domestic water well is situated 100 m higher than the St. Ana Lake water surface, while the straight line distance between the well and the lake closest border is smaller than 1 km. This would imply that a groundwater body draining from the well toward the lake had an unrealistically steep hydraulic gradient (more than 10% on the average). An alternative explanation was to assume an impervious rocks barrier, completely separating the two underground flow systems associated to the Mohoş and St. Ana craters.

Such a hypothesis is consistent with the only conceptual model published so far concerning the hydrological behavior of St. Ana Lake

(Gâştescu & Driga, 1983): the model stipulates that only rainfall and runoff accumulated over the inner slopes of the former crater contribute to the lake recharge; hence – implicitly – no significant groundwater supply occurs. Such an interpretation is also in accordance with the very low electrical conductivity of the lake water (15.7–28.0 μS/cm^2, for 5.80–6.82 pH values – Campean *et al.*, 2012), such conductivity values being very similar to those of rainfall water.

2. INFORMATION PROVIDED BY MAJOR AND TRACE ELEMENTS DISSOLVED IN THE ANALYZED WATERS

By analyzing dissolved major and trace elements, additional information can be acquired on the surface water and groundwater regime in the Ciomadul volcano area. Relevant in this respect proved to be the chemical analyses of several water samples collected from St. Ana Lake, Mohoş peat bog and the domestic well located in its proximity. The concentration determinations have been performed by the Water Geochemistry and Analytical Chemistry Laboratory of the “Emil Racoviţă” Institute of Speleology of the Romanian Academy.

The chemical facies indicated by the major constituents content of St. Ana Lake and of the domestic well is typical for freshwater bodies, namely calcium bicarbonate (the prevalent ions are Ca^{2+} and HCO_3^- – Fig. 2). And as well, the corresponding pH values are near-neutral (7.4 for the lake and 7.1 for the well).

In contrast, the water of Mohoş crater lake is acid (pH 3.7) and of sodium sulfate (Na^+_SO_4^{2-}) chemical facies (Fig. 2). Such features are indicative of local inflows of volcanic origin hydrogen sulfide (H_2S), that is subsequently oxidized to result the “acid sulfate” water type.

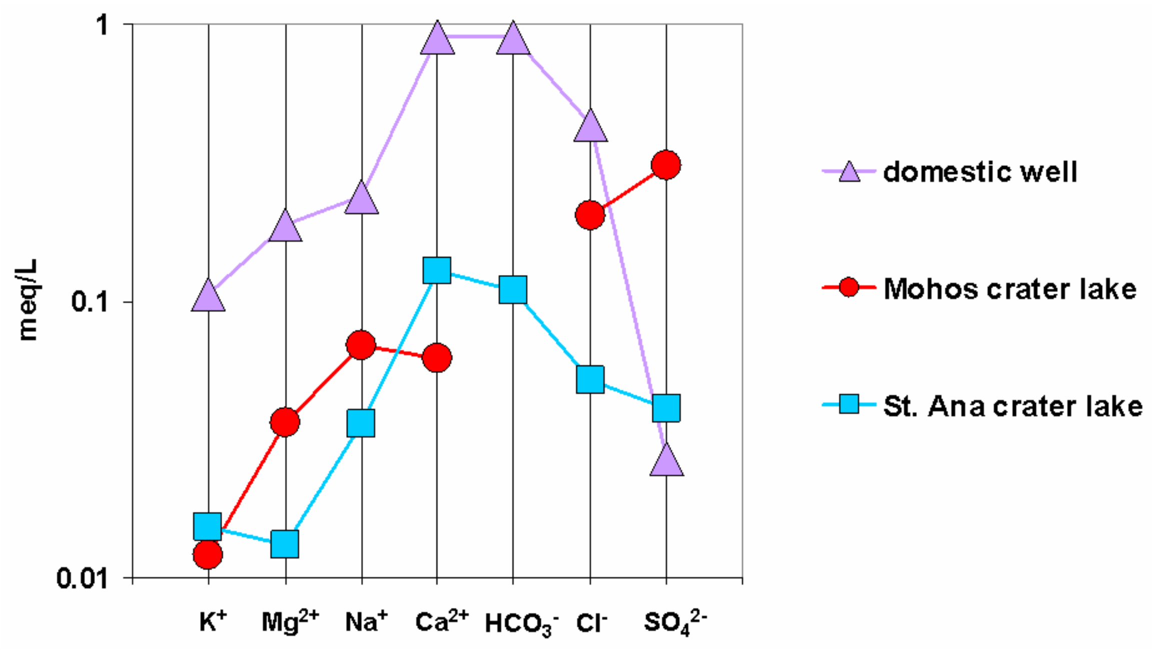

Figure 2 – Schoeller diagram illustrating the relative contents of the major chemical constituents dissolved in the analyzed water samples.

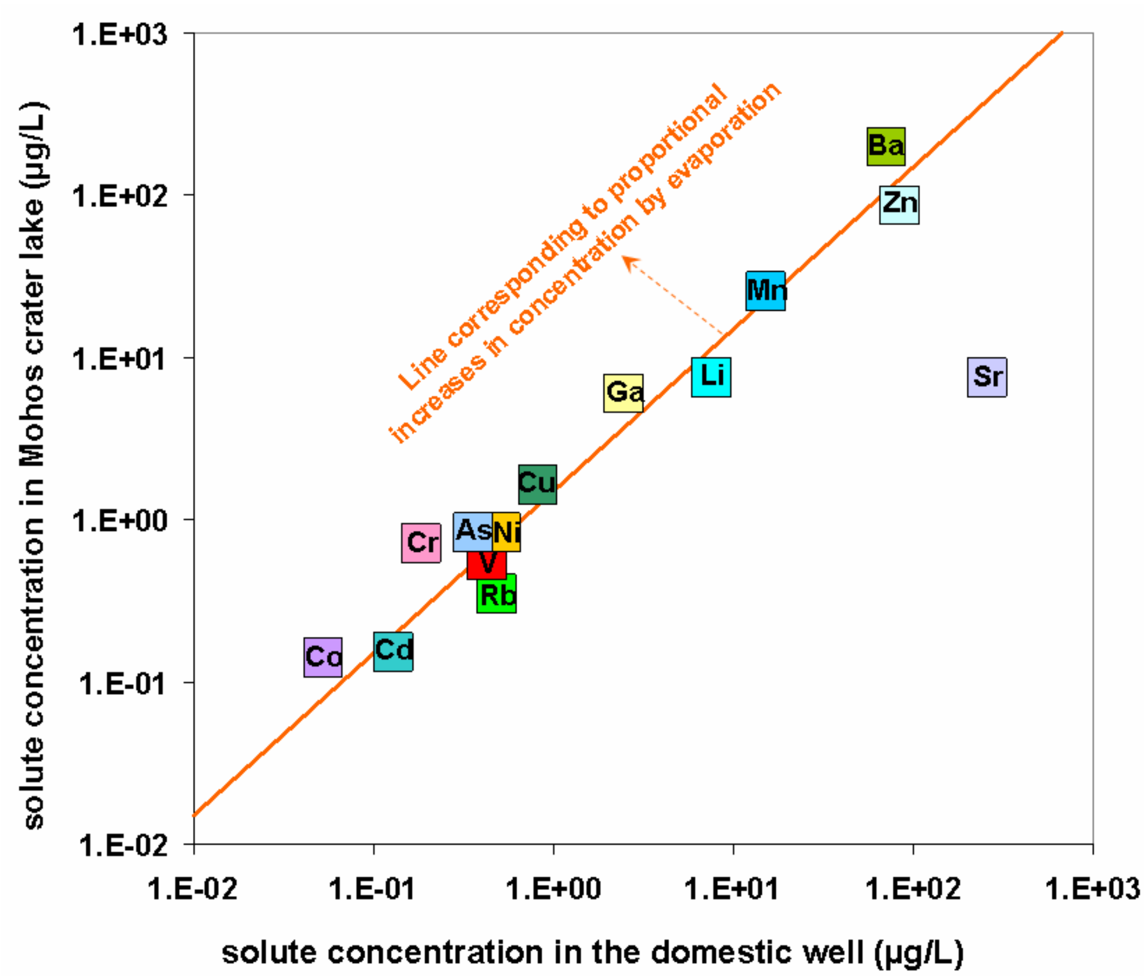

Figure 3 – Trace element concentrations in Mohoş crater lake, plotted as a function of the same trace element concentration in the nearby domestic well.

In Figs. 3 and 4, the trace elements concentrations determined for each of the two crater lakes, St. Ana and Mohoş respectively, were plotted as a function of the corresponding concentrations determined for the domestic well water. Both accordingly constructed diagrams indicate that most data points plot close to the line corresponding to proportional increases in concentration in response to evaporation: accordingly, it is suggested that the concerned chemical elements were uptaken in each of the three aqueous solutions by means of a similar process – namely, by dissolution of the igneous rocks substratum. Subsequently, the concentrations of all elements in the surface water bodies (St. Ana and Mohoş lakes) increased proportionally, ensuing to evaporation.

Yet as compared to the data points' general trend, of plotting close to the equal concentration line, considerable deviations were recorded in the case of two elements:

1. Strontium (Sr) is significantly less concentrated both in St. Ana Lake, and in Mohoş peat bog, with respect to the domestic well water. Rouwet *et al.* (2009) have noticed that El Chichón volcano (Mexico) crater lake was similarly depleted in Sr, as compared to nearby spring water. The suggested explanation was that sediments on the lake bottom had reached an advanced state of alteration,

which largely resulted in removal of mobile elements (Sr in particular), that were initially available for dissolution.

2. Lithium (Li) is considerably less concentrated – by about two orders of magnitude - in St. Ana Lake, as compared to the domestic well water; accordingly, since the Li concentration in the well is virtually equal to that of Mohoş peat bog, the latter is implicitly enriched in Li with respect to St. Ana Lake. Given that Li is a very mobile element, present in the magma degassing products (Pasternak & Varekamp, 1994; Taran *et al.*, 2008), the observed Li distribution could indicate an inflow of magmatic gas in the Mohoş peat bog area, whereas no such inflow occurred next to St. Ana Lake. Such an interpretation is also consistent with the previously stipulated hypothesis, according to which the groundwater flow system associated to Mohoş crater is separated from the system associated to St. Ana Lake by an impervious barrier.

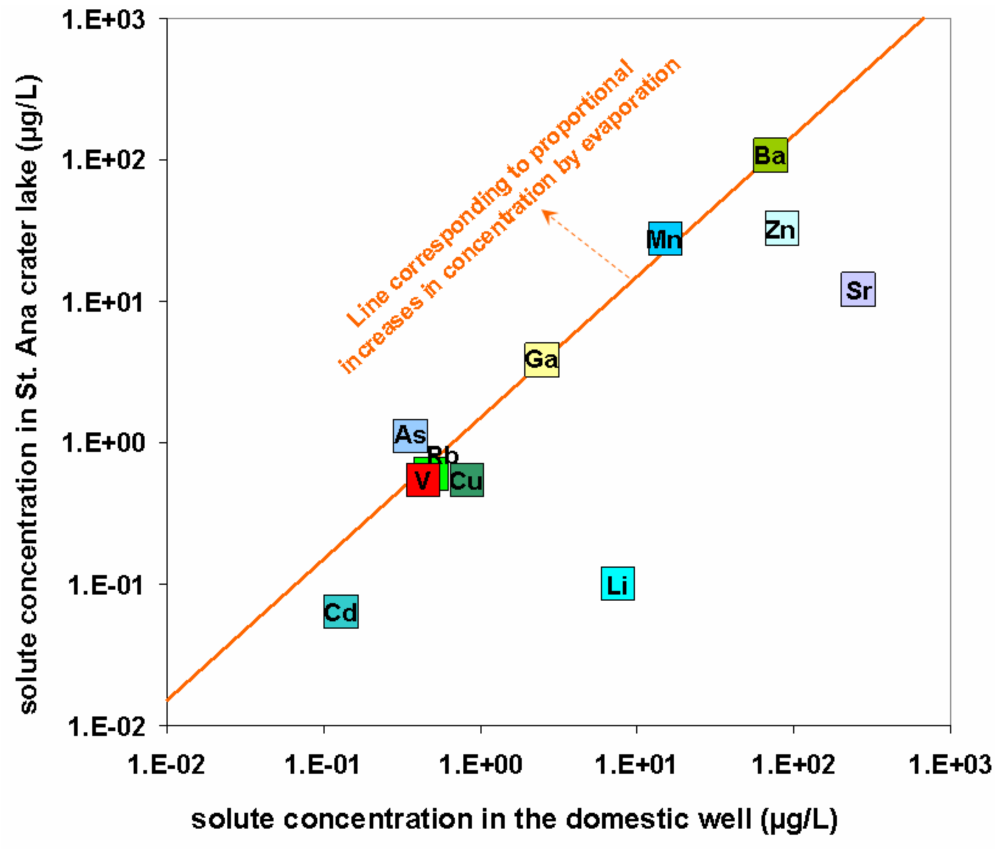

Figure 4 – Trace element concentrations in St. Ana crater lake, plotted as a function of the same trace element concentration in the domestic well located near Mohoş peat bog.

3. CONCLUSIONS

Within the presently extinct Ciomadul volcano, water samples have been collected from several sites (St. Ana Lake, Mohoş peat bog and a domestic well in its proximity). The samples chemical analyses have generally outlined a common chemical signature, that resulted, most likely, following the dissolution of a common substratum of igneous rocks.

A few significant differences between the two crater lakes have also been identified:

– Mohoş peat bog contains acid sulfate water, an indication that sulfidic gas inflows (likely of volcanic origin) enter the lake bottom; in contrast, St. Ana Lake contains calcium bicarbonate freshwater, with no signatures of volcanic fluid inputs.

– Although the minor and trace elements content of the two lakes is rather similar, Mohoş is strongly enriched in Li as compared to St. Ana: additional evidence is thus provided for the absence of deep-origin volatile inputs in St. Ana crater. Moreover, Li enrichments recorded in the aquifer tapped by the sampled domestic well confirm that magma degassing products enter also the groundwater close to Mohoş peat bog.

At the same time, both crater lakes are significantly depleted in Sr. It is accordingly suggested that the sediments on the lakes bottom have been subject to considerable alteration, which resulted in the removal of Sr that was originally present in the leached rock formations.

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