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GEOCHEMICAL CLUES ABOUT A DEEP RESERVOIR THAT SUPPLIES SALINE FLUIDS TO GROUNDWATER OUTFLOWS IN THE SOUTH-EAST CARPATHIANS (ROMANIA)

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ABSTRACT

The East Carpathians Bend region includes a multitude of natural discharges of saline groundwater. Some of these outflows - such as the mud volcanoes at Beciu and a couple of springs at Lepşa - have previously been shown to be sensitive to the intense seismic activity which developed in that area. Yet no attempts have so far been made for exploring relationships that possibly existed between those brines chemical characteristics, and the local geo-structural setting: the latter consists of a stack of successively overthrust nappes, that are built up mainly of Cretaceous and Neogene flysch deposits, with the most external thrust front being partly overlain by formations deposited subsequently (since the Sarmatian) in the Carpathians Foreland. All considered brines have a Na-Cl character and their overall chemical facies is, as well, quite similar (i.e., the concentration ratios of all the main chemical constituents are comparable). In addition, the Sr^{+}/Ca^{2+} ratio is - both for Beciu, and for Lepşa - very large (0.21-0.23); much larger than, for instance, the seawater Sr/Ca ratio of 0.019. Overall, this seems to indicate, besides a Sr enrichment process, a common provenance for all those saline fluids. The latter inference is however rather unexpected, if one takes into account that the Lepşa springs discharge from formations belonging to the so called "Marginal Folds" nappe, while the Beciu mud volcanoes occur within the Foredeep deposits, and that the horizontal distance between those two sampling sites is about 60 km. Still a presumed common reservoir might be hosted by another – so called "Subcarpathian" - nappe: the latter is overlain - in the normal succession of the overthrust units - by the Marginal Folds nappe which hosts the Lepşa springs; while the Subcarpathian nappe most external (eastward) section is covered by Foredeep deposits from which the Beciu mud volcanoes discharge. At the same time, Mg-Li geothermometer assessments indicate that the initial temperature of the Beciu brine supplied by the inferred deep-origin reservoir could amount to 160°C: accordingly, that reservoir depth would be 4.8 km - which is consistent with the position occupied by the Subcarpathian nappe in the concerned region.

Keywords: saline groundwater, mud volcano, chemical facies, Mg-Li geothermometer, South-East Carpathians

INTRODUCTION

The SE Carpathians Bend region is well-known for being subject to an intense and occasionally destructive seismic activity, related to the intermediate depth (60-180 km) Vrancea earthquakes. At the same time, many NaCl type groundwater discharges occur in that region - the most notorious among such outflows being those associated with mud volcanoes close to Buzău town. In the present study, the chemical composition of the brine discharged at Beciu - one the four distinct mud volcano fields of that area – is compared with the composition of a couple of isolated saline springs located some 60 km to the NNW, at Lepșa.

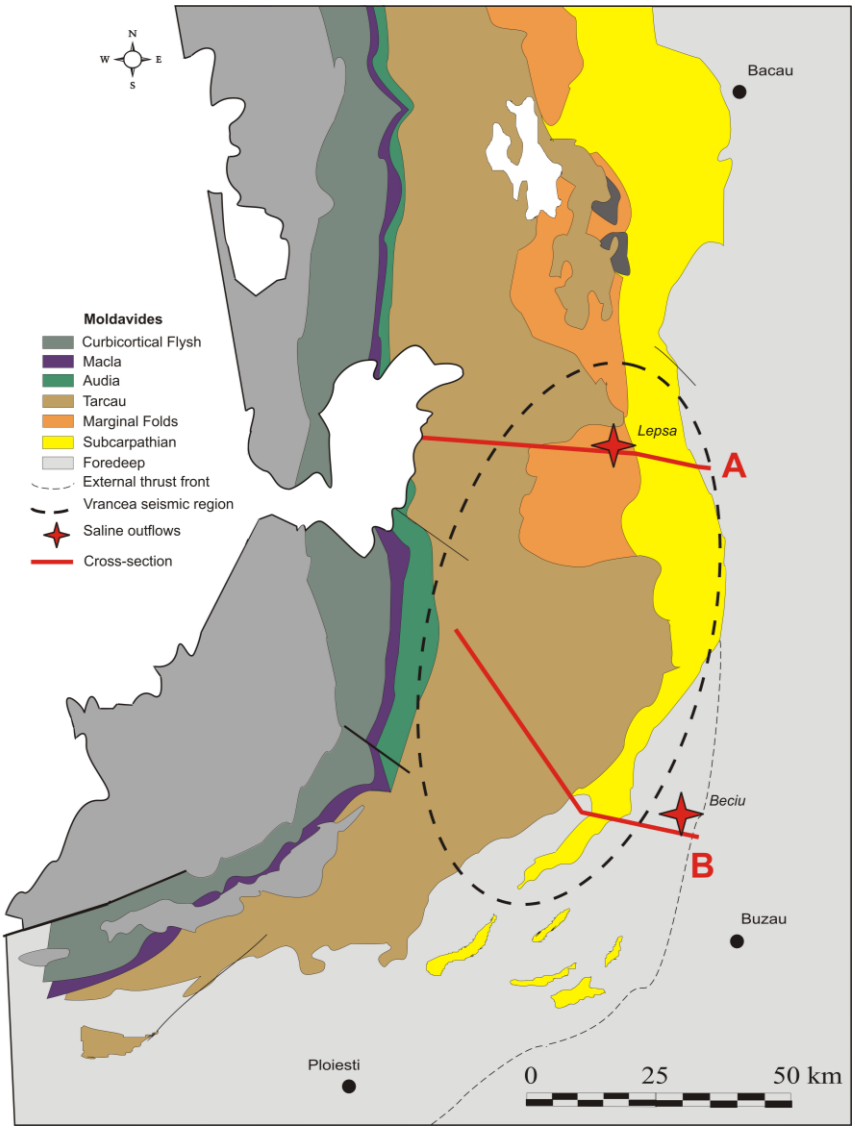

Figure 1. Geological map of the East Carpathians (according to [1], simplified), also indicating the locations of the sampled saline groundwater discharges. Geological cross-sections along the indicated transects are illustrated in Figure 4.

GEOLOGICAL AND HYDROGEOLOGICAL SETTING

The investigated saline springs at Lepşa discharge (Figure 1) from formations belonging to the Marginal Folds nappe, which is built up of tubiditic and other clastic deposits ranging in age from Early Cretaceous to Early Miocene [1].

The Marginal Folds nappe is thrust over the Subcarpathian nappe: the latter includes [2], within its Oligocene to Early Sarmatian age molasse-type sediments (shales, sandstones, marls and conglomerates), also two Early Burdigalian and Badenian evaporitic horizons (salt, gypsum), as well as Badenian volcanic tuffs.

Formations deposited in the Carpathians Foreland subsequently to the nappes system Late Miocene emplacement, overlie, to a large extent, the external thrust front [3]. This is also the case of the mud volcanoes region (Figure 1): there, the most external (Subcarpathian) nappe is overlain by the Foreland deposits, whose lithology is as well of molasse type (shales, sandstones, marls and conglomerates). The latter formations also host a hydrocarbon accumulation (Berca-Arbănaşi) which supplies CH_4-dominated gas emissions that fluidize - together with saline water - near-surface sediments, pushing them upwards: as a result, there are generated the cone-shaped mud volcano structures of Buzău area.

In the framework of the present study there have been analyzed: (i) saline fluids discharged by two saline springs at Lepşa, and (ii) the brine which fluidized the sediments ejected by the Beciu mud volcanoes.

Out of the two saline springs sampled at Lepşa, the one which discharges the less concentrated aqueous solution is sufide-rich - being hence designated as the “Sulfur spring”. Alternatively the springflow with the more concentrated aqueous solution is not sulfide-rich, but it releases free gas bubbles – hence its designation as the “Bubbling spring”; unfortunately, the chemical composition of the released gas has not been determined so far.

Both Lepşa springs display seasonal fluctuations of their chemical constituents’ concentrations [4]. It is thus indicated that a common saline end-member is diluted by variable amounts of freshwater of essentially meteoric origin. Quite noticeable deviations from this regular behavior were recorded [4] only before the M 5.8 Vrancea earthquake of 27 Oct. 2004.

The mud volcanoes at Beciu - the northernmost of the four mud volcano fields in Buzău area [5] - discharge from the Carpathian Foredeep deposits. The corresponding degassing activity is quite intense, in spite of the relatively small areal extent occupied by the vents region. On the other hand, this is the only Buzău mud-volcano field where recurrent intensifications of the eruptive activity have been reported [6]:

- in the summer of 1975;
- in November 1976 (up to 1 m high mud column developed for 24 h; a total of ca. 5000 t of mud erupted during 30 days);
- the Mw 7.4 Vrancea earthquake of 4 March 1977 triggered a similar eruption, which lasted for 6 h.

Overall, it was suggested [5] that Beciu could represent the most permeable and the most active of the four Buzău mud volcano fields.

ANALYSIS PROCEDURES

The Hydrogeochemistry Laboratory of the "Emil Racoviţă" Institute of Speleology has performed the chemical analyses of all collected water samples.

For the Lepşa samples, cation concentrations were determined by means of standard flame-atomic absorption spectrometry methods, conducted with a Perkin-Elmer atomic absorption spectrometer model AAnalyst 800, equipped with deuterium arc background correction system. The total alkalinity (expressed as HCO_3) was determined by means of the Gran titration procedure, by using a pH-meter Delta 345 Mettler Toledo. The Cl^- ion was analyzed by argentometric titration (Mohr method) using a Digital burette Jencons Digitrate. The SO_4^{2-} concentrations were determined by turbidimetry, using a UV/Vis Spectrophotometer Cintra 10 GBC.

Alternatively, for the Beciu sample, the concentrations of all considered components – except HCO_3 and SO_4^{2-}, analyzed similarly to the Lepşa samples - were determined by means of Inductively Coupled Plasma Mass Spectrometry (ICP-MS). There was utilized an ICP-MS instrument NexION 300S (PerkinElemer, Shelton, CT, USA), by adopting the standard [7] as main reference.

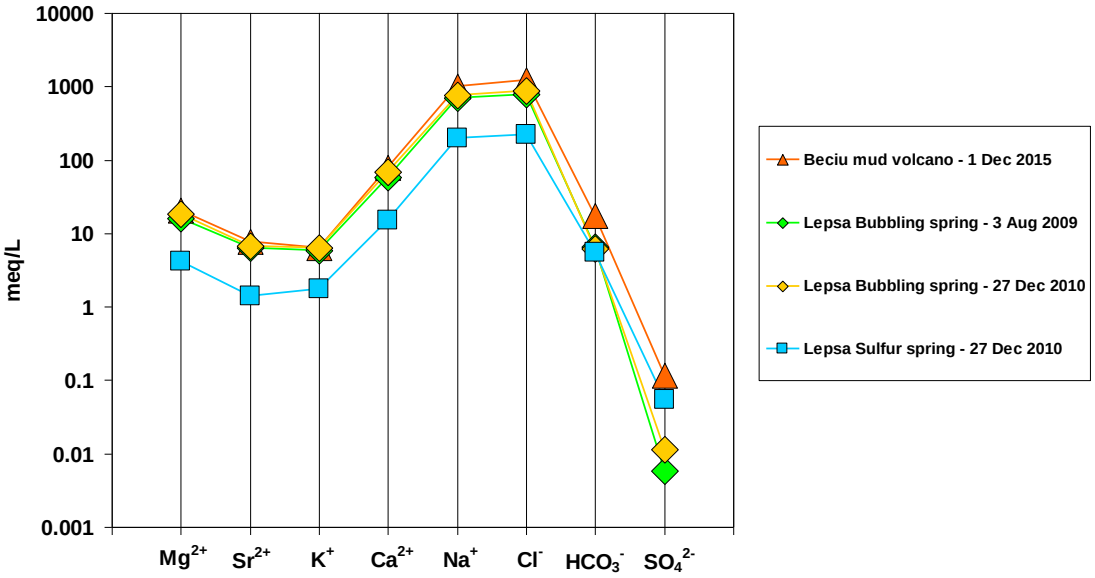

Figure 2. Modified Schoeller diagram illustrating the major constituents' concentrations in the considered outflows.

RESULTS

All sampled groundwaters share several general features: small flow-rates (10^{-3} – 10^{-2} L/s); high TDS contents (up to 52 g/L at Lepşa; up to 72 g/L at Beciu); near-neutral pH (between 5.8 and 7.0 at Lepşa; 6.9 at Beciu); temperature exceeding by a few degrees C the local multi-annual air-average (and thus suggesting up-flow from significant depths).

The modified Schoeller diagram (Figure 2) indicates that all considered brines have a Na-Cl character. Moreover, despite the fact that the Lepşa springs discharge from the Marginal Folds nappe formations, while the Beciu mud volcanoes occur within the

Foredeep deposits, a remarkable similarity can be noticed in terms of chemical facies between the groundwaters collected from those two sites which are located about 60 km apart from each other.

Another similarity between the two sets of discharged brines becomes apparent when the concentrations of Ca^{2+} are compared to those of Sr^{+2} (an element which replaces Ca^{2+} in minerals, by diadochy). For all sampled outflows, the corresponding data points plot, in the log-log diagram of Figure 3, on the same "unitary slope line" (that corresponds to dilution of mineralized water by zero-concentration freshwater): it hence appears that all samples derive from a common saline parent-water, which is subject to freshwater dilution, in variable ratios. Moreover, the corresponding Sr^{2+}/Ca^{2+} mass-ratios are, both for the Beciu and for the Lepşa outflows, very large (0.21-0.23): much larger than, for instance, the seawater ratio of 0.019; hence a strontium enrichment process is mirrored by all concerned fluids.

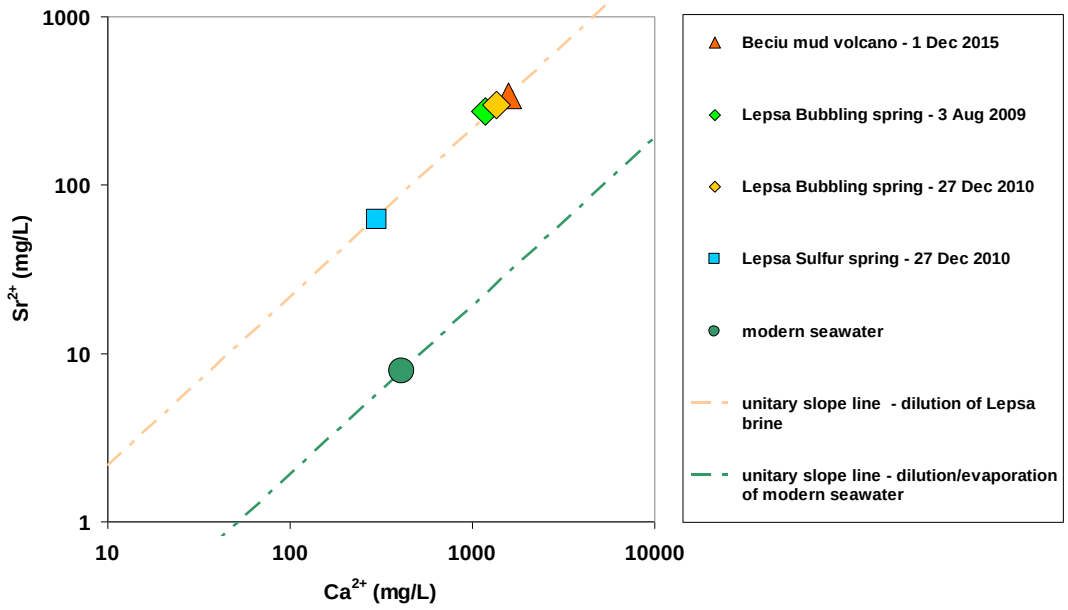

Figure 3. Log-log plot of the considered outflows Sr^{2+} concentration vs. the corresponding concentration of Ca^{2+}.

CHEMICAL GEOTHERMOMETRY

Given the availability of Li analyses for the Beciu saline discharge, the corresponding deep-reservoir temperature was estimated by means of the Mg-Li geothermometer [8], which is known to be applicable to concentrated brines. The concerned geothermometer equation is:

$$t = \frac{2200}{\log\left(\frac{\sqrt{Mg}}{Li}\right) + 5.47} - 273.15$$

where *t* is the temperature (°C) at which the brine had chemically equilibrated at depth, and *Mg* and *Li* are the discharged fluid concentrations of magnesium and lithium respectively (expressed as mg/L).

The accordingly computed temperature for the Beciu brine, 160°C, was next assumed be the bound down to which there could be extrapolated a linear thermal profile recorded [9] in a nearby oil well. The depth value obtained as a result, 4.8 km, likely represents the depth of origin of the saline groundwater discharged by the Beciu mud volcanoes.

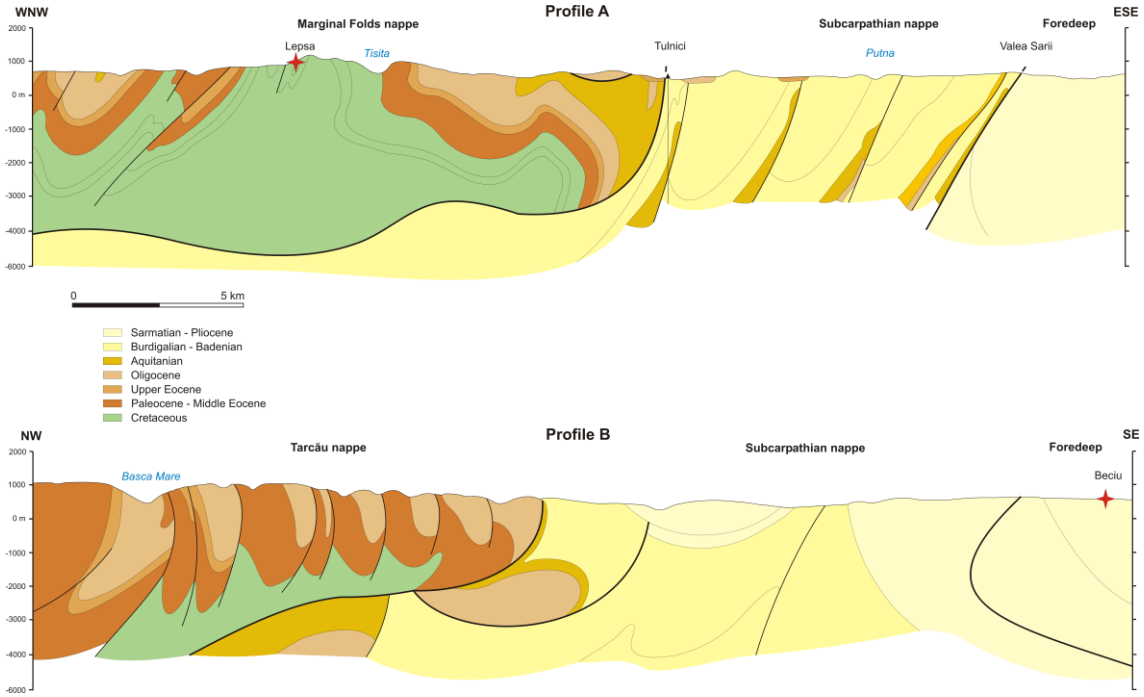

Figure 4. Geological cross sections within the concerned area (after [10], modified). Locations of the profiles in Figure 1.

DATA INTERPRETATION

The chemical similarity noticed between the saline groundwater discharged at Beciu, on one hand, and at Lepşa, on the other, might be explained by a common provenance. For instance, a corresponding common reservoir could be located in the Subcarpathian nappe: that nappe underlies (Figure 4) the Foredeep deposits from which the mud volcanoes discharge, as well as the Marginal Folds nappe which hosts the Lepşa spring. The 4.8 km reservoir depth estimated for Beciu is also consistent with the Subcarpathian nappe position.

Local fractures, crossing - at Beciu - the Foredeep formations, and - at Lepşa - the Marginal Folds unit, likely convey to the ground surface fluids derived from that deep reservoir. At the same time, one cannot exclude the possibility that that the association of such deep-reaching hydrological circuits with the concerned saline outflows is responsible for the "seismic sensitivity" which the latter display.

CONCLUSIONS

Brines sampled from the Beciu mud volcanoes and from a couple of springs at Lepşa display:

- comparable relative contents of the main chemical constituents (hence a similar chemical facies);
- similar Sr^{2+}/Ca^{2+} ratios - that, moreover, are abnormally large (suggesting a Sr^{2+} enrichment process).

Overall, this seems to indicate a common provenance, despite the fact that (i) the Lepşa springs are located about 60 km away from the Beciu mud volcanoes, and (ii) the Lepşa springs discharge from Marginal Folds nappe formations, while the Beciu mud volcanoes occur within the Foredeep deposits.

An inferred common reservoir could be located in the Subcarpathian nappe: that nappe underlies the Foredeep deposits from which the Beciu mud volcanoes discharge, as well as the Marginal Folds nappe which hosts the Lepşa springs.

Mg-Li geothermometer assessments indicate that the Beciu brine temperature in the inferred deep-origin reservoir could amount to 160°C: accordingly, the reservoir depth would be 4.8 km - which is consistent with the position occupied in that region by the Subcarpathian nappe.

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