Potential occurrence of alkaline waters in ophiolites from Banat and Apuseni Mountains (Western Romania)

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Abstract. The basic and ultrabasic rocks included in the ophiolitic massifs may strongly influence the chemical features of waters, that may become alkaline (pH higher than 8), or even hyperalkaline, with pH above 10. The present contribution emphasizes the theoretical framework on the possible presence and distribution of alkaline waters in some ophiolitic areas from Romania. Field investigations have been performed in Almăj Moutains (Tișovița area), where alkaline waters with pH around 9 have been found in several springs. The predominant hydrochemical type in the investigated water sources is Mg-HCO_3. The current contribution also aims to preliminary assess the potential of the Southern Apuseni Mountains region to yield alkaline waters, taking into account that a significant part of this unit consists of ophiolitic rocks covering more than 1000 km^2. The area of interest overlaps numerous areas included in Natura 2000 network, condition that may also provide better protection for the potential water sources.
Key Words: alkaline water, Banat Mountains, Apuseni Mountains, ophiolites, GIS.

Introduction. Alkaline and hyperalkaline waters present growing interest from both a scientific and practical point of view. Alkaline waters, with pH between 7 and 8, sometimes even higher, but generally not exceeding 9, are quite common, being related to carbonate rocks, which are important suppliers of alkalinity. In carbonate areas, the Ca-HCO_3 water type, with more or less Mg is generally met. It is well known the ability of carbonate rocks to neutralise acidity. Based on these properties, limestone, that is relatively cheap material, is extensively used to neutralize acidic water generated in the mining areas by acid mine drainage (Santofimia & López-Pamo 2016). The ophiolitic rocks also show neutralizing potential, although they are less used for this purpose and they were subject to fewer studies (*e.g.* Jonckbloedt 1998). As an example, in Zlatna mining area (southern Apuseni Mts.) Papp et al (2017) have shown the contribution of the ophiolitic bedrock to the neutralization of the acid mine waters. In ophiolitic areas with alkaline waters, the Mg-HCO_3 type predominates in most of the cases.

The extreme alkalinisation of natural waters to pH values over 10 or even exceeding 11 or 12 (hyperalkaline) is a complex process which is not yet understood in every detail. It generally occurs in relation with ophiolitic massifs, and it is probably associated with active serpentinization of ultramafic rocks. The water chemistry dramatically changes in hyperalkaline environments, where the Mg-HCO_3 water type is replaced by the Ca-OH type (Barnes et al 1967). Recent works have shown a direct link between the occurrence of hyperalkaline waters and the production of abiotic methane (e.g. Etiope et al 2016). According to current global research, there are several areas that have hyperalkaline springs from serpentinites. Countries with such areas are: Italy, Greece, Portugal, Bosnia, Serbia, Bulgaria, Jordan, Cyprus, Oman, Philippines, New Caledonia, Mexico, West USA (Boschetti et al 2012).

Basalt is another type of rock recognized for its ability to generate alkaline waters. In a research conducted in Brazil (Serra Geral Aquifer), alkaline waters with a pH up to 9.9 were found. The geological substratum of the studied area is predominantly basaltic (Gastmans et al 2016). The capacity of basaltic rocks to increase the pH of water is also reported in a study conducted in Israel (Möller et al 2016).

Alkaline water is considered a good adjuvant in reducing hyperacidity in the digestive system. Koufman & Johnston (2012) have outlined some potential beneficial effects of alkaline water consumption (pH 8.8) on people with gastric reflux problems. Although there are few studies analysing the effects of alkaline water on the human health, or demonstrating its benefits, during the recent years a worldwide increase in the consumption of this type of water is observed. Numerous alkaline water brands are commercially available. Additionally, various water-alkalizing machines (Kangen type) have been produced.

The current contribution proposes an overview of the potential of the main ophiolitic areas in Romania to generate alkaline waters. The study is focused on the Banat and Apuseni Mountains, which are the regions of maximum extent of the ophiolites in Romania.

Geological background of the main ophiolitic areas in Romania. Two main areas with ophiolites are known in Romania, one has been associated to the Variscan orogeny, while the second belongs to the Alpine cycle.

The first, conventionally named in this work Tisovita area, is located in the south-western part of the country, in the Almăj Mountains (Southern Carpathians) on the left bank of the Danube River. The structure is interpreted as remnants of a Devonian back-arc basin. Based on petrographic features, the Tisovita ophiolitic complex is divided in two zones. The Eastern zone consists of harzburgites, dunites with podiform chromitites, mafic cumulates and lavas, while the Southern zone includes mafic (gabbros) and ultramafic (dunites and serpentinites) cumulates (Plissart et al 2009). During our multiple field surveys in Tisovita area, starting from 2012, the main types of rocks have been observed. The most frequent rocks are dunites and associated ultrabasic rocks, with different degrees of serpentinization. Very often, the rocks are completely serpentinized, so that the genuine rock cannot be recognized anymore. Asbestos-rich serpentinites have been mined in the past through shallow workings, starting from the outcrops. Chromite is relatively abundant in the fresher rocks in some areas, and has been extracted in the past in small underground mines.

The second large ophiolitic area corresponds to the Southern Apuseni Mountains, which represent the northernmost occurrence of the East Vardar ophiolites. The terminal segment of this belt is displaced from the general NW-SE direction of the Dinaric ophiolites, being oriented SW-NE in the Mures area, and continues beneath the Transylvanian Basin. Some small outcrops are found in the Eastern Carpathians (Boev et al 2018). Three evolutionary stages have been distinguished in the magmatic activity that formed the ophiolitic complexes in the Southern Apuseni Mountains (Ianovici et al 1976). The most active magmatic areas have migrated from South-West to North-East during the time period Middle Jurassic to Lower Cretaceous. The earliest magmatic activity occurred in the Lower to Middle Jurassic and has produced a thick pile of basaltic lavas. Also gabbros and peridotites are present. The second stage (Upper Jurassic – Neocomian) has generated various types of pyroclastic rocks, including basalts, andesites, limburgites, dacites, etc. The third stage (Barremian –Aptian) has generated basalts and spilites.

Alkaline waters in the study areas. In Tisovita area, the groundwater resources are scarce, and few springs have been identified. Several small streams are flowing, generally following a north-west to south-east direction. The physico-chemical parameters of waters were measured in the field, by using a WTW Multi 350i multimeter. The pH of water in the streams is around 8.5, with some variations, probably depending on the abundance of precipitations. In springs and old abandoned mining tunnels, the pH is around 9.0, sometimes exceeding 9.5. The electrical conductivity ranges between 500 and 800 µS cm^{-1}, as a consequence of the low mineralization of the water, as shown in the Schoeller plot (Figure 1). The ionic composition of water was determined by using a Dionex ICS1500 Ion Chromatograph. The dominant ions are HCO_3 and Mg. Calcium may occur in comparable amounts to Mg in some of the water sources (Figure 1).

In the Southern Apuseni area, the currently available experimental data are scarce for the moment, so that the current study has a predictive character. The types of rocks that outcrop in the area offer good arguments for the potential occurrence of alkaline waters. The main interest would be on the western part of the ophiolitic area, where more ultrabasic rocks are located (peridotites and some olivine-bearing rocks).

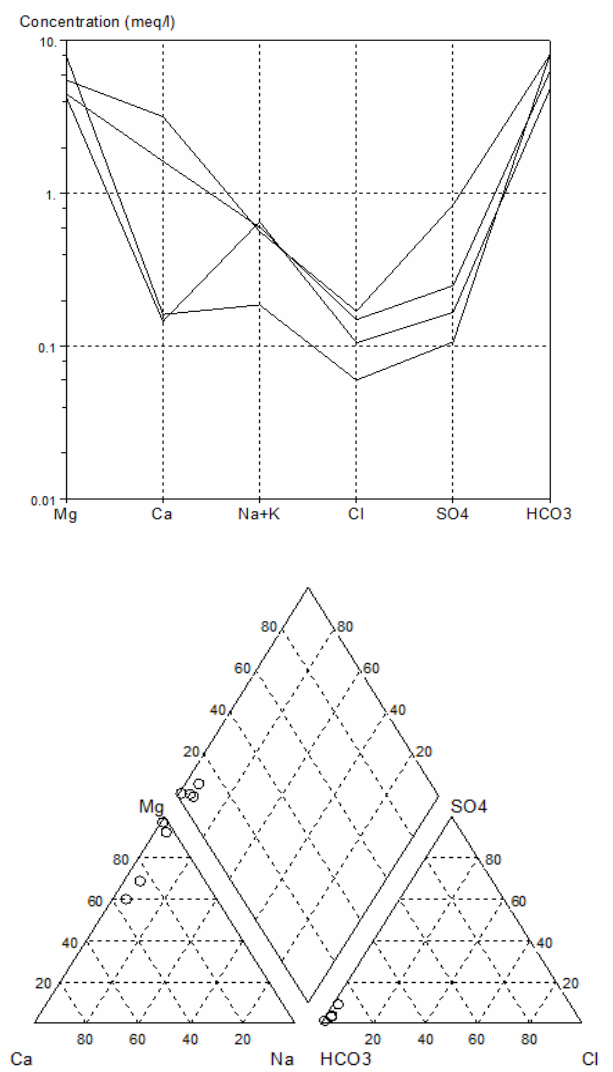

Figure 1. Schoeller (up) and Piper (down) plots illustrating the major ions composition of water from several sources in Tisovita area.

Spatial analysis. We tried to better define the area of interest in the Apuseni Mountains by using Quantum GIS, which was helpful for the spatial analyses and construction of maps included in the present article. The digitization of ophiolites within the study area has been done manually. From the geological map of Romania (raster) 1:200,000, a vectorial map of the areas that contain ophiolites was generated (Figure 2). This map was then overlaid with other vectorial layers and more complex maps were created. The generated numerical data was also analysed using Quantum GIS. The specific tools in the Attributes table were used for calculating the area of interest and to determine the dispersion of the study specific rocks.

Some statistical data were obtained consequently to the digitization of the areas that contain ophiolites in the Apuseni Mountains. The area of interest for the present study expands over approximately 108,000 ha. This area is formed of 161 subzones ranging from less than 1 ha to 65,680 ha. The highest fragmentation is located in the eastern part of the study area, while the western part is very compact regarding the ophiolite zones.

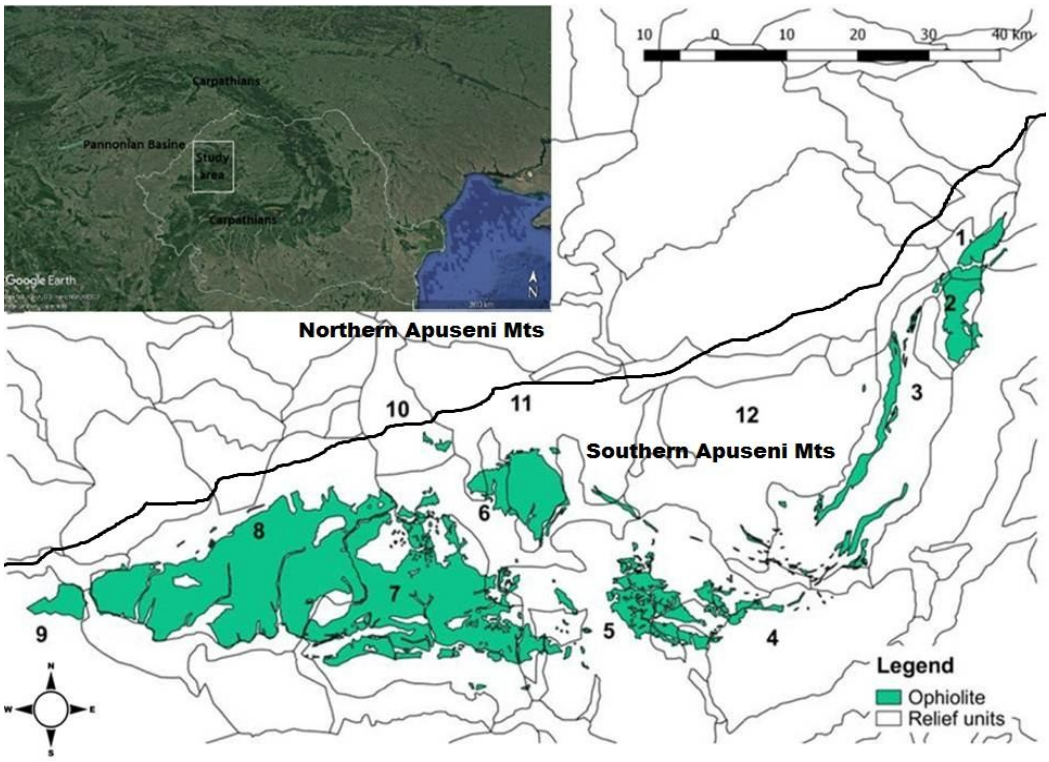

Figure 2. Ophiolite distribution within the morphological units of the Southern Apuseni Mountains: 1. Hășdate, 2. Colții Trascăului, 3. Bedeleu, 4. Ampoiului unit, 5. Săcărîmbului unit, 6. Brad Depression, 7. Măgureaua Mts., 8. Husului Mts., 9. Lipovei Plateau, 10. Halmagiu Depression, 11. Gaina Mt., 12. Detunatelor Mts.

To facilitate the theoretical study, as well as part of the practical study, the generation of a thematic map that highlights the distribution of ophiolites within morphological units was necessary. The area of interest expands over 19 morphological units, represented by 9 depressions: Trascău Depression, Zlatna Depression, Meteș Depression, Almaș-Bălașa, Băița Depression, Brad Depression, Halmagiu Depression, Conop Depression and Câmpia Turzii Depression. The high relief units within the area of study are: Hăjdatea Peak, Colții Trascăului, Bedeleu Peak, Detunatelor Mountains, Ampoiului Mountains, Scarîmbului Mountains, Găina Mountain, Măgureaua Mountains and Hușului Mountains. The Aiud Hills is another unit of interest for the present study.

The area of study expands over four counties: Cluj, Alba, Hunedoara and Arad. The largest surface in which ophiolites can be found is located within Hunedoara County. Arad County has the second largest area with ophiolites, as well as the most compact ophiolite areas, while Cluj and Alba counties have the smallest areas with ophiolites.

In most of the cases, ophiolites are rocks with low permeability, thus the probability of forming important aquifers is low. Generally, the yield of the springs in ophiolitic areas is very low. The waters flowing through ophiolites will likely be alkaline, of Mg-HCO_3 type. When the ophiolites are intercalated with other rock types, such as limestones for example, the general groundwater circulation may be facilitated.

At the same time, dilution may occur, thus diminishing the pH and possibly modifying the original chemical composition of the water. However, the contacts between the carbonate massifs and the ophiolite complexes could be favourable for generating good quality alkaline waters, and also sufficient yields for the bottling industry. This situation is presumably common in the Apuseni Mts., as in the eastern part of the study area (Hășdate, Trascău, Bedeleu) the ophiolites are covered by thick piles of Jurassic limestones. A detailed hydrogeological survey is necessary in order to confirm this assumption and to a identify the best spots for the possible future valorisation of the water resource.

In other regions of Romania, ophiolites occur on relatively small areas in the Eastern Carpathians and on Mehedinți Plateau. No data are currently available on the influence of these bodies on the hydrogeological features in the respective areas. Beyond the Apuseni Mountains, basalts can be found in some geological units of Romania, as the Perșani Mts. High pH values are expected, as in basaltic complexes in Israel the pH ranges between 8.0 and 8.85 (Möller et al 2016). The permeability of basalts is low, as the pores resulted during the degassing of the magma are generally not interconnected. The columnar separations where present, may provide pathways for the circulation of water. Alkaline waters with pH over 9 have been reported from several localities with mineral waters in Romania, some of them used for therapeutic purposes (Table 1). These waters are generally salty, rich in sodium, chloride and sulphur or sulphate (IBF 1961-73).

Table 1

Alkaline waters with pH above 9 in non-ophiolitic areas from Romania

County	*Site*	*pH*	*Major ions and general chemical features*
Valcea	Govora (Spring no. 6)	9.27	Na, high S, Cl, HCO_3, low SO_4, hypertonic water
Braila	Movila Miresii (Lake)	9.60	Na, Cl, SO_4, very high TDS
Iași	Lețcani (Spring)	9.50	Na, K, HCO_3, low Cl, hypotonic
Vaslui	Drînceni-Ghermănești (Well no. 5)	9.32	Na, S, Cl, I, hypotonic

Source: IBF (1961-1973).

Conclusions. Alkaline waters represent a topic of growing interest for the hydrogeological research from a theoretical and practical point of view. They are common in the ophiolitic areas, containing basic and ultrabasic rocks. Two main areas with ophiolites are known in Romania, the Variscan massif from Tisovița (Almăj Mts.) and the Southern Apuseni Mountains, corresponding to the northern extremity of Vardar ophiolitic belt. Some other areas with ophiolities and basaltic complexes are less extended. Several sources with alkaline water (pH around 9) have been identified in Tișovița area. Their hydrochemical type is mainly Mg-HCO_3, characteristic for the weathering of the ophiolitic rocks. No hyperlkaline sources (pH > 10, Ca-OH type) have been found. The Southern Apuseni Mountains represent a prospective area for the alkaline waters. The Jurassic limestones on top of the ophiolites in the eastern part of the area can be of interest for the existence of well-developed aquifers. A systematic hydrogeological survey would be necessary in order to determine the potential of the proposed areas to produce alkaline waters in sufficient amounts to be extracted.

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