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# Composition and origin of mine water at Zlatna gold mining area (Apuseni Mountains, Romania)

Delia Cristina Papp[a,1], Ioan Cociuba[a], Călin Baciu[b], Alexandra Cozma[b]

[a]Geological Institute of Romania, 1 Caransebeș Street, Bucharest, 012271, Romania
[b]Babes-Bolyai University, Faculty of Environmental Science and Engineering, Cluj-Napoca, Romania

**Abstract**

Hydrochemical and isotopic characterization of mine water having connections with groundwater and surface water at Zlatna gold mining area (Apuseni Mountains, Romania) was performed to provide insights on mine site emissions with the surrounding environment after the cessation of mining operations. The mine water coming into direct contact with mineralization is more acidic than the mine water that only interacts with the host rock. Light isotopic composition of most mine water suggests snowmelt and high altitude precipitations as the main source of recharge. Linear correlation between $\delta D$ and $\delta^{18}O$ values indicates that all water sources belong to the meteoric cycle. For most mine water sources no significant seasonal variations of the $\delta D$, $\delta^{18}O$, pH and TDS values was recorded, indicating well-mixed underground systems and slow flow recharge pathways. Other mine water sources show seasonal variations of these parameters suggesting continuous recharge of mine water and a fast underground circulation. No relevant contamination of springs and phreatic water by mine water could be revealed, suggesting different underground pathways for the two types of water. On the contrary, running water is contaminated by mine water and the negative effects of acid mine drainage occur mainly in the summer months when the debit of the running water decreases.


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## 1. Introduction

Here we report the hydrochemical and isotopic characterization of mine water and background water from a post-mining environment of a gold deposit in Romania (Zlatna mining area, Apuseni Mountains) to assess mine water sources, flow paths and interactions with surface water.

* Corresponding author. Tel.: +4-074-474-075; fax: +40-314-033-499.
*E-mail address:* deliapapp@yahoo.com


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Isotope applications in mine settings include[1]: assessment of groundwater flow models and sources of recharge, tracking of mine water inflows and outflows, assessment of water-rock interactions, as well as assessment of mining effects on groundwater and surface water. The results of several previous isotopic studies[2,3] indicated that mine water is not immediately derived from precipitation or from rapid and direct infiltration of groundwater. Mixing with waters of different origins, water/rock interaction processes, and effects of evaporation can occur and modify the initial δD and $\delta^{18}O$ signature of recharge source.

## 2. Study area and geological framework

Zlatna gold mining area (approx. 40 $km^2$) is located in the Metaliferi Mountains of the South Apuseni mountain range (Romania) and belongs to the "Golden Quadrilateral" mining district (900 $km^2$) which hosts some of the richest gold and silver deposits in Europe.

During Alpine tectonic orogeny of the South Apuseni Mountains, several major extensional regimes occurred which caused magmatic and metallogenic events[4]. During the Middle Jurassic – Early Cretaceous, ophiolites and island arc calc-alkaline volcanites with base metals ± gold mineralization were generated. During Middle - Upper Miocene, volcano-tectonic events occurred as a consequence of Tisia block rapid extrusion and clockwise rotation. The Late Cretaceous - Paleogene calc-alkaline magmatites contain Au-Ag and Au-Ag-Pb-Zn-Cu mineralization. The Badenian-Pannonian dominant calc-alkaline magmatism has related porphyry epithermal Cu-Au (Mo) and epigenetic vein hydrothermal mineralization. The volcanic activity had two peaks at 14.6-10.77 Ma and 9.3-7.4 Ma[5]. Quartz andesite with amphibole and pyroxene, and quartz andesite with amphibole and biotite are the main petrographic types. Basalt andesites occurred at the end of magmatic activity.

In the study area, the basement is made up of Jurassic ophiolites. At their upper part, sporadic intercalations of jasper and radiolarite or Middle Jurassic limestones can be found. The sedimentary cover, with a thickness of few hundred meters, consists of Late Jurassic – Hauterivian reef limestones, found only on restricted areas, followed by a suite of detrital formations, Cenomanian - Early Turonian in age. The detrital formations have a dominant pelitic character. The overlying Badenian molasse formations are unconformable and include: (1) the Fața Băii Formation (Early Badenian) made up of conglomerates, sandstones, clays and marls; (2) the Almașul Mare Formation (Middle Badenian) made up of gravels, reddish clay sandstones, gypsum lenses, limestones, and red marls, and (3) the volcanogenic sedimentary formation (Late Badenian) made up mainly of blackish gray marls with gypsum and salt lenses. At its upper part, tuffs, andesite breccia, and sandstone with plant fragments also occur.

From a hydrogeological point of view, the area (elevation range of 420 – 1100 m) is a medium-precipitation area (~ 480 – 700 mm/year), with a snow cap that lasts for 2 - 3 months in the winter. The average annual temperature is 10.5°C, with a maximum monthly average of 28°C during the summer period, and minimum monthly average of –5°C during the winter. The density of the hydrographical network is about 1 km/$km^2$. In Zlatna gold mining area the extraction activities were completely abandoned in 2007. Presently, the mine openings are secured, but significant flow of acid mine water continues to discharge into the river system.

## 3. Sampling and analytical methods

Water samples (12 sources of running water, 9 springs, 3 domestic wells and 8 sources of mine water) were collected on a monthly basis from January to December 2015. The running water sources were sampled both upstream of the discharge point of mine water and downstream. For each water source the following parameters were determined in the field: pH, temperature, and TDS. Water samples were collected for laboratory analyses to determine the hydrogen and oxygen isotopic composition, as well as the major ion content.

The chemical and isotopic analyses were performed at the Babeș-Bolyai University, Cluj-Napoca, Romania. The isotopic composition of hydrogen and oxygen was determined using a Picarro CRDS L 2130-I with autosampler. Two internal standards calibrated using standards provided by IAEA Vienna were used. The precision of the $\delta^{18}O$ and δD measurements is ±0.12‰ and ±0.8‰, respectively. All isotopic data are expressed in conventional δ notation as the permil deviation of D/H ratios with respect to the V-SMOW standard. Major ions were analyzed using ion-exchange chromatography.