

Geochemical and isotopic investigations on the thermal and mineral underground waters from the Republic of Moldova

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Republic of Moldova (RM) has a large spectrum of underground mineral waters (16 reservoirs) of eight principal aquifers, most of which affected by contaminants originated by natural sources and anthropogenic activities. Inorganic natural tracers and stable isotopes are useful tools to fingerprint the water source and solutes, respectively. The aim of this investigation was to determine the geochemical and isotopic features of the most important thermo- and mineral waters from RM to trace their flow pathways and evaluate the presence of deep fluid sources discharging from fault systems, developed in response to the structural setting of the area. To the best of our knowledge, no systematic geochemical investigations were previously carried out in this area. RM has an area of 33,840 km² and lies within the East European Precambrian Platform, two structural and/or stratigraphic layers, which are distinguishable in basement and sedimentary cover in the northern and central part of country. The basement rocks include granites, gneisses and gabbros. The sedimentary cover, overlying the crystalline basement, is almost undeformed and consists of Upper Proterozoic, Mesozoic and Cenozoic rocks. The geological structure is like a matrix formed from different layers of rocks consisting of permeable and impermeable strata. The deep aquifers are situated down to 1,000 m depth from the bottom to the top: Vendian (Ediocarian) and crystalline basement rocks, Silurian crystalline limestone, Cretaceous limestone, Baden-Sarmatian limestone and clay-sand deposits, middle Sarmatian limestone and clay-sand layers. Other younger aquifers were not investigated. In this framework, 54 samples from the most important underground reservoirs of RM were collected and analyzed for major, trace species and dissolved gases. An inventory of isotopic (¹⁸O/¹⁶O and ²H/¹H ratios in water and ¹³C/¹²C in dissolved CO₂) features (including tritium units in selected samples) was also provided. By a geochemical point of view, the Moldavian waters showed neutral to alkaline pH, Total Dissolved Solids between 515 and 75,846 mg/L and mostly negative Eh values. They displayed a relatively high variability in terms of composition, being classified as Ca(Mg)-HCO₃(SO₄), Na-Cl and Na-HCO₃. In the mineralized waters from the Baden-Sarmatian aquifer, trace element distribution revealed significant anomalies for F⁻, I⁻ and Br⁻ (up to 13.2, 23.7 and 140.5 mg L⁻¹, respectively). Moreover, high values of As and Ni were found in the Dubasari waters (up to 13.8 μg L⁻¹ and 43 μg L⁻¹, respectively). Dissolved gases were mainly dominated by N₂ (from 0.16 to 0.78 mmol/L), while CO₂ and CH₄ were between 0.02 and 0.66 mmol/L and 0.00005 and 0.44 mmol/L, respectively. Oxygen and hydrogen isotopic ratios were ranging from -15.8 to -0.9 ‰ (V-SMOW) and from -104.5 to -32.8 ‰ (V-SMOW), respectively, suggesting a meteoric source slightly modified by prolonged water-rock interactions. Carbon isotopes in dissolved CO₂ were very variable (¹³δ-CO₂ from -25.2 to +2.8 ‰), the most positive values being associated with the waters collected from the oil field in the southernmost part of the country. Finally, water ages by using tritium units (presently in progress) will be used to trace the flow of the youngest waters.