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## Hydrogeochemical characterization of the waters circulating in the seismically active area of the Pesaro-Urbino province (northern Marche, central Italy)

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The Province of Pesaro-Urbino (northern Marche, central Italy) represents one of most seismically active areas in Italy, since it is interested by the presence of two major composite seismogenic sources: i) the first one is located in the Umbria-Marche Apennines; ii) the second one is along the Adriatic coast from Cattolica to Ancona cities. This area has recently experienced an intense seismic activity, e.g., the 1781 “Cagli Earthquake” with a magnitude of 6.4  $M_w$ , and the 1930 “Senigallia Earthquake” of 5.8  $M_w$ . The last earthquake (5.5  $M_w$ ) occurred on November 9, 2022, with its epicenter located in the Adriatic Sea, 35 km away from the city of Pesaro. Since the geochemical knowledge of this area is limited, a large-scale sampling survey was carried out during spring and autumn 2022. A total of 87 samples were collected from different types of emergencies (i.e., cold springs, wells, mineral springs, sulfur springs and ditches) and various geological and tectonic-structural contexts. The study area is dominated by a complex sedimentary structure (e.g., limestones, clays and alluvial deposits) and by climatic and topographic conditions that may influence the chemical and isotopic composition of the investigated fluids. A detailed geochemical characterization is thus of paramount importance in order to define a geochemical background. The aim of this study was to (1) understand the possible interaction of deep-originated fluids and shallow aquifers and (2) evaluate the use of selected geochemical parameters as possible seismic tracers. The results showed the presence of five different geochemical facies: (i) calcium-bicarbonate waters with low TDS (<500 mg/L); (ii) calcium-bicarbonate waters with a strong enrichment in sulfate (up to 200 mg/L); (iii) waters with extreme sodium-carbonate composition and an alkaline pH (>8.8); (iv) calcium-sulfate waters; and (v) sodium-chloride waters. The water isotopic composition showed a clear meteoric origin for all the investigated samples. The composition of major dissolved gases showed two different compositional clusters: (a)  $N_2$ -dominated gases with  $N_2/Ar$  ratios similar to those of air and ASW (Air Saturated Water); (b)  $CO_2$ - and  $CH_4$ -rich gases pertaining to mineral and sulfur springs. The origin of  $Ca-HCO_3$  waters is almost exclusively related to the dissolution of carbonate minerals. On the contrary,  $Ca-HCO_3(SO_4)$  waters are probably originated by deep circulation pathways and interactions with the Upper Triassic Burano Formation, composed by anhydrite layers. The

Ca-SO<sub>4</sub> waters should be considered as the product of ongoing flows within Miocene gypsum formations, whilst Na-HCO<sub>3</sub> waters as the consequence of long-lasting interactions between meteoric waters and silicate rocks (containing albite) in saturation/oversaturation conditions for carbonate-bearing minerals. Finally, the Na-Cl waters probably derive from mixing processes between meteoric and highly saline connate waters trapped into the foredeep clayey deposits. Therefore, the Ca-HCO<sub>3</sub>(SO<sub>4</sub>) and Ca-SO<sub>4</sub> waters can be regarded as the most interesting fluids to be monitored for a geochemical network aimed at recognizing chemical and isotopic variations related to seismic activity. They are indeed showing a deeper hydrogeological pathway and appear to be less influenced by surface processes.