

Application of multiple isotope systematics to unravel water-rock interaction processes and hydrological pathways in seismically active areas towards the deployment of a water monitoring network aimed at seismic surveillance

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Waters circulating in the seismically active Pesaro-Urbino province (central Italy) were investigated to understand water-rock interaction processes and groundwater pathways through a multi-isotopic approach. The aim was to select specific sites to be included in a water monitoring network for seismic surveillance intended at recognizing seismic tracers.

The geochemical composition of groundwaters reflects their complex story underneath: the hydrologic and hydrogeologic features such as recharge-discharge mechanisms, flow velocity and water movement within the aquifers, together with the assessment of the lithological features, are fundamental aspects to be considered for establishing a monitoring network aimed at seismic surveillance. In this context, the application of multiple isotope systematics (C, S, O, H, B, Sr) plays a crucial role. In fact, the isotopic data make it possible to trace the primary sources of some solutes, or the secondary processes affecting the waters during their underground circulation, also allowing to identify the geological formations interacting with the circulating waters along their paths.

The investigated waters show various compositions (Ca-HCO₃, Ca-SO₄, Ca-HCO₃-SO₄, Na-HCO₃). Water geochemistry and isotopic contents suggest that Ca-HCO₃ waters interact with limestones and silicates at shallow depths. Contrarily, Ca-SO₄, Ca-HCO₃-SO₄ and Na-HCO₃ waters relate to longer water-rock interaction and/or deeper circulation patterns within the aquifers. All the waters show $\delta^{13}\text{C-TDIC}$ values mainly biogenically-derived, with $\delta^2\text{H-}$ and $\delta^{18}\text{O-H}_2\text{O}$ fingerprints suggesting a meteoric origin. By combining $\delta^{34}\text{S-SO}_4$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios we recognized that Ca-HCO₃-SO₄ and Ca-SO₄ waters interact with the evaporitic Triassic Burano formation constituting the regional basal aquiclude, suggesting long and deep flow paths. This makes these waters interesting to be monitored for seismic

tracers, being likely able to carry possible deep seismic signals (e.g., deep-sourced gases inflow, enhanced metals mobility). Contrarily, Na-HCO₃ waters are characterized by $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\delta^{11}\text{B}$ values approaching those of the siliciclastic Marnoso Arenacea Fm, consistent with long-lasting interactions with Na-bearing silicates. Our results suggest that the hydrogeochemical and multi-isotopic approach provided paramount information to detect sites more prone to record possible geochemical variations during the build-up phase of seismic events, making it suitable for being applied to other seismically active areas.