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Hydrogeochemical Constraints on Deep Fluid and Carbon Transport in the Roccamonfina Volcanic Area across the Tyrrhenian–Apennine transition zone (central–southern Italy)

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Hydrothermal fluid circulation in quiescent volcanic and post-volcanic regions controls the transport of chemical and thermal fluxes through the crust. At the Roccamonfina volcanic complex (Campania–Lazio boundary, central-southern Italy), two main degassing areas were identified, reflecting: i) residual magmatic activity and/or ii) ascent of deep fluids along active fault structures. We conducted a comprehensive field-based hydrogeochemical survey, collecting waters and gases from deep and shallow wells, springs, and natural vents. Samples were analysed for major ions, dissolved gases, helium isotopes (R/Ra), and δ^{13}C-TDIC, and integrated with gas–water–rock interaction modelling and carbon and heat mass balance calculations constrained by karst aquifer properties. Our results show a southward increase in mantle-derived helium, delineating the transition between Roman and Campanian magmatic provinces. R/Ra values up to 1.87 in the northeastern caldera sector indicate a significant deep contribution, slightly lower than in more active volcanic areas such as Campi Flegrei. Cold and hypothermal carbonate springs transport ~505 t/day of deep-carbon (δ^{13}C up to ~0‰) and ~78 MW of cumulative thermal flux. The spatial distribution of gases and isotopic signatures highlights fluid ascent along regional fault networks, correlated with areas affected by recent seismic swarms. These findings demonstrate that direct measurements of waters and gases in karst and volcanic aquifers provide unique insights into deep fluid dynamics, fluid–rock interactions, and thermal–chemical fluxes. The study emphasises the role of groundwater-mediated degassing as a key process in volcanic–extensional settings, illustrating how karst aquifers act as natural pathways linking deep magmatic processes to surface geochemical outputs.