

Fluid Geochemistry vs. Neotectonics: Constraints from the Rapolano Terme Area (Siena-Radicofani Basin, Central-Northern Apennine, Italy)

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Rapolano Terme is located at the eastern boundary of the Siena-Radicofani Neogene Basin (Tuscany, central Italy) and is well known for the intense travertine quarry activity, taking place at least since the Middle Age. These deposits are associated to a large number of thermal spring discharges at which a free-gas phase (mainly CO₂) is commonly related. The low-enthalpy fluid system feeding these springs is presently used for therapeutic purposes, thermal spa or CO₂ extraction from up to 1000 m deep wells whereas domestic utilisation of the geothermal heat is basically missing.

Previous studies in this area (e.g. Fancelli & Nuti, 1975; Duchi et al., 1992) focused their attention to the geochemical characterisation of the main fluid phases. This work reconsiders those studies with a new and detailed collection of thermal, saline and cold waters and free and stripped gases from the Rapolano Terme area aimed to explain the fluid geochemistry in a neotectonic contest. Particular attention has been addressed to study the oxygen, hydrogen and carbon and helium isotopic ratios in water and gases, respectively and the relation between deep and shallow aquifers. The composition of thermal waters (mainly Ca(Mg)-HCO₃ with rare Na(K)-Cl waters) is related to mixing processes between a deep, hot (Ca(Mg)-HCO₃-SO₄) and a shallow cold (Ca(Mg)-HCO₃) component at which a third, connate (Na(K)-Cl), component may be added when thermal discharges emerge in the inner western part of the basin where thickness of the Neogene sediments is higher. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in the waters indicate a meteoric origin for both the cold and the thermal discharges, although some CO₂-rich waters have negatively shifted $\delta^{18}\text{O}$ values with respect to the Global Meteoric Water Line. This is possibly related to isotopic exchange reactions favoured by either long-term interaction between CO₂ and H₂O or high gas/H₂O ratios as already observed in other areas (e.g. Négrel et al., 1999).

The CO₂-rich deep fluids, possibly originated by thermo-metamorphic reactions involving Mesozoic limestones and crystalline Paleozoic (Duchi et al., 1992; Minissale et al., 1997), mainly uprise along NW-SE-oriented fracture system and mix with the meteoric aquifer present at shallow depth. As a consequence, the resulting gas composition is marked by high contents of CO₂ (up to 99% by vol.) and progressive percentages of atmospheric components such as N₂ (up to 10%), O₂ (0.0005 to 0.45%), Ar (0.0007 to 0.4%) and Ne (up to 0.0003%). H₂S, H₂, CH₄ and light hydrocarbons (pertaining mainly to the alkane C2-C5 group) contents are due to decomposition reactions involving organic matter entrapped in the shallow sediments.

The $\delta^{13}\text{C}$ in CO₂ (-5.21 to -9.21 per mil PDB) and the ³He/⁴He ratios (0.08 to 0.99), expressed as R/Ra where Ra is that in the air, indicate a crustal origin for the deep fluid phase. The extremely low contents of mantle-originated ³He are possibly related to a compressive tectonic regime presently acting in the Siena-Radicofani basin. This hypothesis seems to be in good agreement with the Plio-Quaternary structural geology evidence observed in numerous Apennine basins (Boccaletti et al., 1999 and references therein).

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