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Geochemical signature of permanent and ephemeral thermal springs in Val di Cornia, Central Italy

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In the Val di Cornia area, several permanent thermal springs outflow. They belong to the hydrothermal system of Campiglia Marittima and have been exploited since longtime for the therapeutic properties of the discharged waters. With an average outflow of 250 L/sec, Calidario (36.3±0.2˚C) is the most important permanent spring of the area. Periodically, i.e. about every 10 years, a number of ephemeral thermo-mineral springs in Bagnarello (46±0.2˚C) and Monte Peloso (42.2±0.3˚C) area, spontaneously reactivate over short time periods (several weeks to few months), with a maximum discharge of 150±20 L/sec. This phenomenon is generally induced by intensive rainfall events.

In this contribution, we present new geochemical analyses of waters discharged from Calidario and the ephemeral springs reactivated at the beginning of 2001 and at the end of 2010. These new data are then compared to previous analyses to investigate geochemical variations over a 30-years period.

Both ephemeral and permanent thermal springs have Ca-SO_4 geochemical signature, typical of groundwaters circulating through the carbonate-evaporitic complexes of the Tuscan Nappe (Mesozoic age). Clear salinity trends are identified, with TDS increasing from Calidario to Monte Peloso and Bagnarello springs, up to a maximum of about 3000 ppm.

Chemical speciation indicates that most of the thermal waters are close to saturation with respect to fluorite and gypsum/anhydrite, with solute geothermometers indicating possible equilibrium temperature of 50-55˚C for Monte Peloso and Bagnarello waters, respectively. Higher temperatures, up to 75˚C, were inferred by assuming equilibrium at depth with the aluminosilicates of the regional Basement (phyllitic formations of Paleozoic age), below the evaporites of the Tuscan Nappe (Triassic age).

With δ^{18}O and δ^{2}H values of –6.4 (±0.2)‰ and –38.9 (±2.9)‰ respectively, the ephemeral springs have a steady stable isotope composition, comparable to permanent thermal springs. Based on these data, the main recharge area has been hypothesized in correspondence of outcropping carbonate formations in the hilly region NE of the area under study. The lack of tritium (^{3}H) at Bagnarello suggests the existence of long underground residence times for the hydrothermal component, whereas the presence of measurable amounts of tritium at Calidario indicate the contribution of rapidly infiltrating meteoric waters. The ^{87}Sr/^{86}Sr ratio of ephemeral and permanent thermal springs (below 0.70804), significantly lower than local Ca-HCO_3 groundwaters (0.70889), indicates a prolonged interaction with Mesozoic carbonate and evaporitic formations (0.70789). The δ^{34}S-SO_4 signature (+15.4‰) mirrors the isotopic composition of local evaporites, reinforcing on the hypothesis of extensive thermal circulation through the Tuscan Nappe.

Overall, the geochemical signature of the thermal springs of the Campiglia Marittima hydrothermal spring appears stable over the period 1984-present. Geochemical data support a regional groundwater circulation scheme where thermal waters move along a preferential NE-SW direction, flow at different depths within Mesozoic carbonate and evaporite formations, and emerge in correspondence of main faults.