



Water and gas geochemistry of the Calatrava Volcanic Province (CVP) hydrothermal system (Ciudad Real, central Spain)

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An extensive geochemical and isotopic investigation was carried out in the water and gas discharges of the Late Miocene-Quaternary Calatrava Volcanic Province (CVP) (Ciudad Real, Spain) with the aim reconstruct the fluid circulation in the area. CVP consists of a series of scattered (monogenetic) vents from where alkaline lava flows and pyroclastic deposits formed in two different periods. The first stage (8.7-6.4 Ma) mainly included ultrapotassic mafic extrusives, whilst the second stage (4.7-1.75 Ma) prevalently originated alkaline and ultra-alkaline volcanics. Both stages were followed by a volcanic activity that extended up to 1.3 and 0.7 Ma, respectively.

This area can likely be regarded as one of the most important emitting zones of CO₂ in the whole Peninsular Spain along with that of Selva-Emporda in northeastern Spain (Cataluña) and it can be assumed as one of the best examples of natural analogues of CO₂ leakages in Spain. This latter aspect is further evidenced by the relatively common water-gas blast events that characterize the CCVF. In the last few years the presence of a CO₂-pressurized reservoir at a relatively shallow level as indeed caused several small-sized explosion particularly during the drilling of domestic wells.

The fluid discharging sites are apparently aligned along well-defined directions: NW-SE and NNW-SSE and subordinately, ENE-WSW, indicating a clear relationship between the thermal discharges and the volcanic centers that also distribute along these lineaments.

The CVP waters are mostly hypothermal (up to 33 °C) and are generally Mg(Ca)-HCO₃ in composition and occasionally show relatively high concentrations of Fe and Mn, with pH and electrical conductivity down to 5.5 and up to 6.5 mS/cm, respectively. The oxygen and hydrogen isotopes suggest a meteoric origin for these waters. The mantle source of these volcanic products is apparently preserved in the many CO₂-rich (up to 990,000 mmol/mol) gas discharges that characterize CVP, whose carbon and helium isotopic signature is characterized by values between -6.8 and -3.2 ‰ (V-PDB) and up to 2.7 R/Ra, respectively. Nitrogen and argon are atmospheric in origin and their contents are up to 11,850 and 313 mmol/mol, respectively, while H₂S and CH₄, despite occurring in the great majority of the CVP samples, have concentrations that rarely achieve 71 and 81 mmol/mol, respectively. It is worthwhile to mention that the N₂/Ar ratios are occasionally characterized by values higher than those of the atmospheric and air saturated water and the respective ⁴⁰Ar/³⁶Ar values are higher than the atmospheric ratio (295.5), suggesting a deep source for these inert gases.