

Anomalous CO₂ contents in a shallow aquifer of the Mt.Amiata geothermal area, Italy

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In the framework of a project funded by Seismic Service of the Tuscany Region [1], the Bagnore thermal spring (Mt.Amiata geothermal area) has been selected as a suitable site to identify possible hydrogeochemical anomalies related to seismic activity. Since 2004, the Bagnore spring ($T_{\text{WATER}} = 21.5^{\circ}\text{C}$) has been monitored in continuous (more than 8×10^5 data available today) with an automatic station equipped for the measurement of temperature, pH, EC, Eh, and the dissolved content of CO₂ and CH₄. During the period 2004-2012, 68 discrete sampling campaigns for the determination of selected chemical-physical parameters in situ (T, pH, EC, alkalinity), and chemical parameters in the laboratory (Na, K, Ca, Mg, Cl, SO₄, NO₃, B), have also been performed. From all these data, it emerges that the low salinity (240 mg/l) waters of the Bagnore spring belong to the Ca-SO₄ chemical type, and are characterized by a background P_{CO2} value of about 0.04 bar. Significant H₂S and H₃BO₃ anomalies have been also detected, suggesting that the shallow aquifer feeding the Bagnore spring effectively absorbs gases diffusing from below. Isotopic analyses on TDIC ($\delta^{13}\text{C} = -7.8$ and -11.6‰) and dissolved SO₄ ($\delta^{34}\text{S} = -6.9\text{‰}$) point to exclude the hypothesis of a prevalently magmatic origin for the gases interacting with waters in the shallow volcanic aquifer. TDIC is thus interpreted as the result of the mixing between CO₂ of metamorphic origin and soil-derived CO₂. Low, basically radiogenic ³He/⁴He ratios in gas vents of the area [2], further support this hypothesis. The $\delta^{34}\text{S}$ -SO₄ signature possibly indicates that H₂S absorbed in the shallow aquifer derives from thermochemical reduction of Triassic anhydrite ($\delta^{34}\text{S} = 15.5\text{‰}$) in the geothermal reservoir, at an estimated temperature of about 300°C.

During the last three years, two anomalous, progressive increases in P_{CO2} (up to 0.07 bar) and SO₄ concentration (up to +10%), correlated with a measurable decrease in pH (up to -0.3 pH units, down to 5.6) and HCO₃ concentrations, have been observed over several months. These trends ended just a few days before two seismic events of magnitude 2.5 and 2.7.

[1] Cioni R. *et al* (2007) *NHESS* 7, 405-416. [2] Minissale *et al* (1997) *JVGR* 79, 223-251.

Origin of the chemical and U-Sr isotopic variations of soil solutions, stream and source waters at a small catchment scale (the Strengbach case; France)

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This is the first comprehensive study dealing with major and trace element data as well as ⁸⁷Sr/⁸⁶Sr isotope ratios and (²³⁴U/²³⁸U) activity ratios (AR) determined on the totality of springs and brooks of the Strengbach catchment. It shows that the small and more or less monolithic catchment drains different sources and streamlets with very different isotopic and geochemical signatures. Different parameters control the diversity of source characteristics. Of importance are especially the hydrothermal overprint of the granitic bedrock, which was stronger on the granite from the northern than from the southern slope, and the different meteoric alteration processes of the bedrock causing the formation of 0.5 to 9 meter thick saprolite and above the formation of an up to 1m thick soil system. The chemical compositions of the source waters in the Strengbach catchment are only to a small extent the result of alteration of primary bedrock minerals and rather reflect dissolution/precipitation processes of secondary mineral phases like clay minerals.

The (²³⁴U/²³⁸U) AR however, are decoupled from the ⁸⁷Sr/⁸⁶Sr isotope system and reflect to some extent the level of altitude of the source. In addition, the important thickness of the saprolite allows to explain the low (²³⁴U/²³⁸U) AR <1, which are uncommon for surface waters. Preferential flow paths along constant fractures in the bedrocks might explain the over time homogeneous U AR of the different spring waters.

At the soil scale, the geochemical signatures of soil solutions result mainly from biological impact (recycling, degradation and exudation), weathering of secondary phases and atmospheric inputs.

This study further highlights the fact that processes controlling the chemical and isotopic water signatures are different at the soil and catchment scales.