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Geochemical monitoring of mantle-derived gases migration along active faults: case of Vapor cave (southern Spain)

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Fluid migration along faults can be highly complex and spatially variable, with channelled flow along karstified structures of the vadose zone. One such example is Vapor cave, near the urban area of Alhama de Murcia, situated along a tectonically active, NE-SW trending master fault as results of the convergence between Africa and the microplate of Iberia. Vapor cave represents an outstanding gases-blowout site from the upper vadose zone, developed in a favourably fissured carbonate-cemented conglomerate host rock under hypogene speleogenesis by the upwelling of hydrothermal (>33°C, and 100% relative humidity) and CO₂-rich air, in or from the zone of fluid-geodynamic influence.

In this study, we investigate the gaseous composition and, specifically, the geochemical fingerprint of deep-origin greenhouse gases (CO₂, CH₄) of both cave and soil air at Vapor cave. Detailed surveys were conducted to monitor the deep-origin gases exhaled by the cave, by using high precision field-deployable CRDS and FTIR spectrometers to in situ and real time measure the concentration and δ¹³C of both carbon-GHGs. Inert gases like radon were also measured in parallel by a pulse-counting ionization chamber (alpha spectroscopy). The collected data provide new insights into the control exerted by active fault segments on deep-seated gas migration toward the surface.

The C species of the deep-origin fluids are dominated by CO₂ (concentration higher than 1% and δ¹³C-CO₂ ranging from -4.5 to -7.5‰) with the abundance of CH₄ below the atmospheric background. It is estimated that the exhaled air represents between 1 to 3% of this pure theoretical CO₂ added from the deep endogenous source feeding the cave atmosphere and linked to the fault activity. Anomalous radon concentrations recorded at this site also confirm the contribution of this geogenic gas in the cave atmosphere (²²²Rn ranges 40-60 kBq/m³ at -30 m depth) and its accumulation in the overlying soil (exceeding 10K kBq/m³).

In contrast to the release of large volumes of deep endogenous CO₂, Vapor cave constitutes an

effective sink of methane (CH_4). The deep-sourced CH_4 is continuously depleted and ^{13}C -enriched along the vertical migration pathway into the cave ($\text{CH}_4 < 1$ ppm and $\delta^{13}\text{C}$ close to -30‰). Some anomalous concentrations of deep endogenous methane have been already registered in the cave air, e.g. during march 2016, with CH_4 ranging 2.3 to 3.4 ppm and $\delta^{13}\text{C}\text{-CH}_4$ lighter than that found in the local background atmosphere. These anomalous CH_4 data could be related to the occurrence of contemporary earthquakes, characterized by a total amount of seismic energy released of 4.9×10^9 J and epicenter locations southwest of the cave and within a radius of 20 km.

The continuous depletion of CH_4 in the cave air constitutes itself a very valuable property in terms of using as potential earthquake precursor in combination with other geochemical indicators. Hence, any anomalous concentration and isotopic deviation of this gas in the cave atmosphere with reference to the background level in the cave atmosphere could denote a more intense migration of endogenous fluids through the upper vadose zone, which could be related with an increase of the regional seismotectonic activity.