Duvalo (North Macedonia): A “volcano” without volcanic activity

Duvalo area is located close to the village of Kosel, in Ohrid region, in the South-western part of the Republic of North Macedonia.
Duvalo is characterized by a natural phenomenon of intense soil degassing.

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Duvalo is considered to be an **active post-volcanic area** by local people, due to the “rotten eggs” smell, sulphur exhalations, strong soil degassing and “eruptions” from “craters”.

*Increased activity reported at the last active volcano in the Balkans - Duvalo, Macedonia*

"Duvalo" represents post volcanic phenomenon located in Kosel, just 7 km north from Ohrid.

Duvalo’s appearance consists of several small craters with a diameter of 0.5m and depth of 30 cm

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But is it really a volcano?

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No volcanic rocks or volcanic activity has been documented in the geologic history of the Kosel area since Early Triassic (Markoski et al., 2018).

The Ohrid area is a seismically active extensional basin, and Duvalo corresponds to an active fault system; thus, the phenomenon can be related to a tectonic origin (Hoffmann et al., 2010).

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A mixing trend, typical of soil gases, between a CO₂-dominated end-member (CO₂ > 96%) of deep origin and the atmospheric air can be recognised. Results of the samples richest in CO₂ are consistent with previous analyses (Trojanoviky, 1925; Iloski et al., 1957; Markovski et al., 2018), which reported that the gases were composed mainly of CO₂ (90-98%) and H₂S (0.8%).
At Duvalo no sign of mantle contribution can be recognised:

- Helium shows a $R/R_A$ ratio of 0.1, which indicates an almost pure crustal origin.
- $\delta^{13}$C-$\text{CO}_2$ values around 0 ‰ also point towards a crustal (marine limestone) source.

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Isotope composition of methane shows:
- $\delta^{13}\text{C-CH}_4$ values range from -36.8 to -34.4 ‰ vs. V-PDB
- $\delta^{2}\text{H-CH}_4$ values vary between -166 and -158 ‰ vs. V-SMOW.

The samples fall within the thermogenic field.

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Hydrogen sulfide is found in the gases with concentrations up to 0.55%. No sign of hydrothermal activity is present in the area. Therefore the most probable origin for \( \text{H}_2\text{S} \) is thermochemical sulfate reduction (TSR):

\[
\text{Hydrocarbons} + \text{CaSO}_4 \rightarrow \text{CaCO}_3 + \text{H}_2\text{S} + \text{H}_2\text{O} \pm \text{CO}_2 \pm \text{altered hydrocarbons} \pm \text{solid bitumen}.
\]

Part of the uprising \( \text{H}_2\text{S} \) is oxidized in the shallower part of the system and the produced sulphuric acid reacts with carbonate rocks producing abundant \( \text{CO}_2 \).

The enhanced permeability within the fault system of the area favours both TSR and \( \text{H}_2\text{S} \) oxidation processes and gas upflow to the surface.
Carbon dioxide flux measurements have been performed with the accumulation chamber method in Duvalo area.

Values up to 23,600 g/m²/d have been measured.

The most exhaling areas are prevailingly aligned in NNW-SSE direction, the same of the main tectonic structures of the area.

The total CO₂ output estimated for Duvalo site is 66.9 t/d.
Duvalo is clearly not a volcano and is neither a hydrothermal feature.
The strong gas exhalation is only related to one of the active tectonic structures bordering the Ohrid graben.

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The enhanced permeability deriving from tectonic activity favours the production at depth of H₂S through thermochemical sulfate reduction.

Hydrogen sulfide, on the way up to the surface is partially oxidized creating acid solutions, which reacting with carbonates, produces abundant CO₂ that is degassed from the soils at Duvalo.

Such processes are so efficient to release to the atmosphere about 25,000 tons of CO₂ each year.