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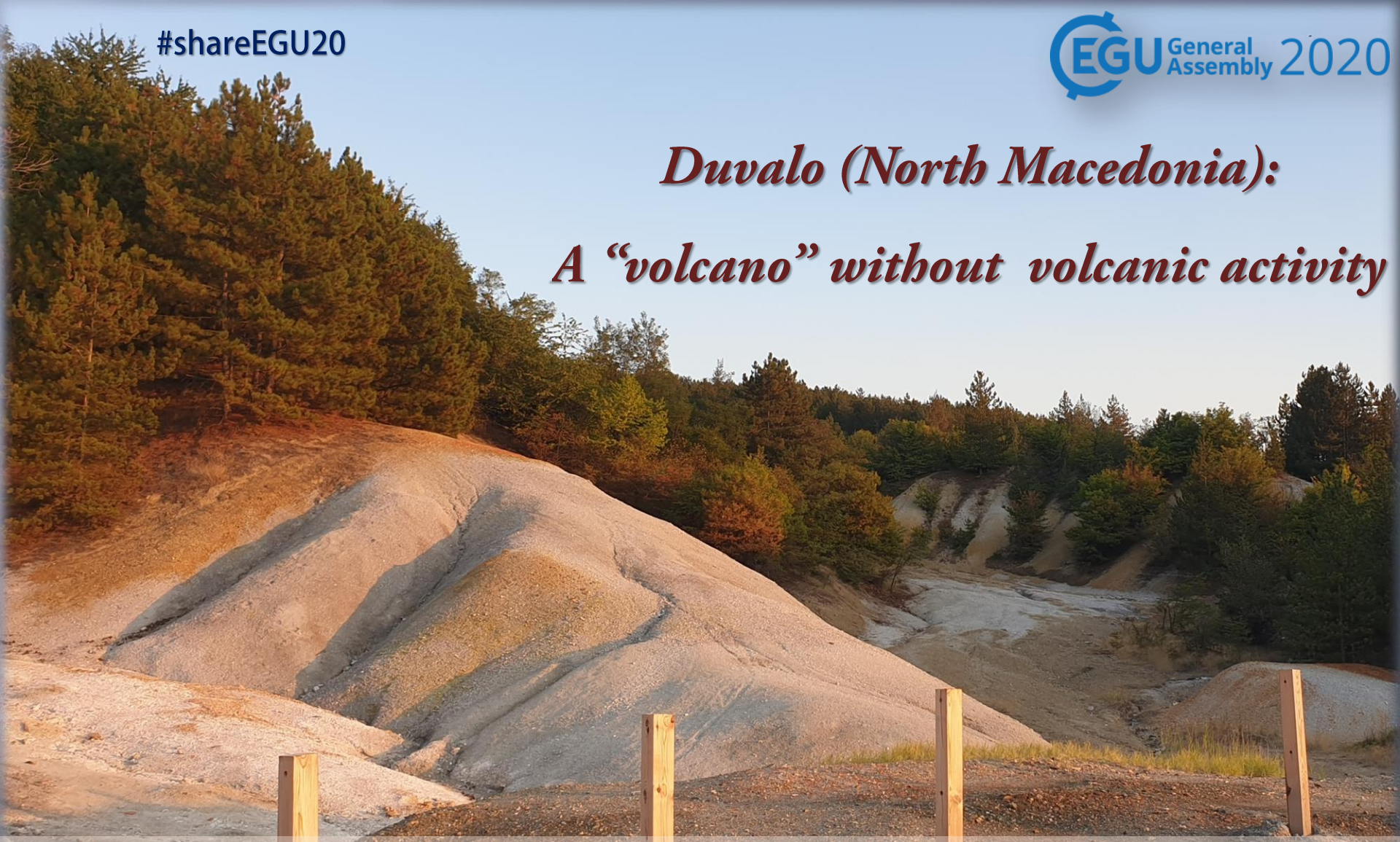
Duvalo (North Macedonia):

A "volcano" without volcanic activity



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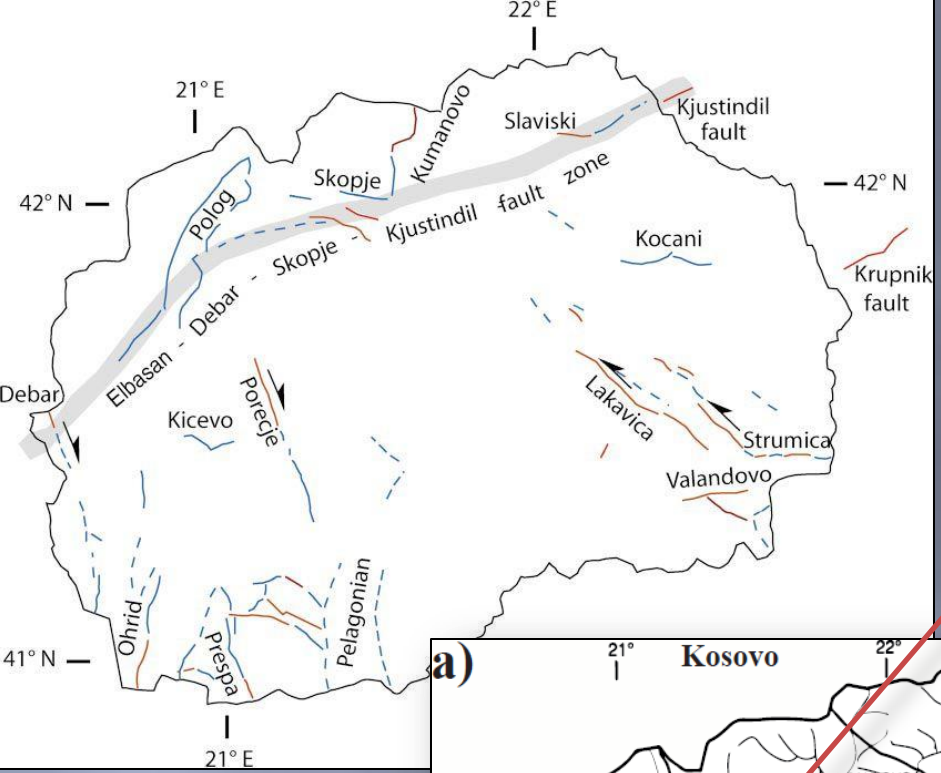
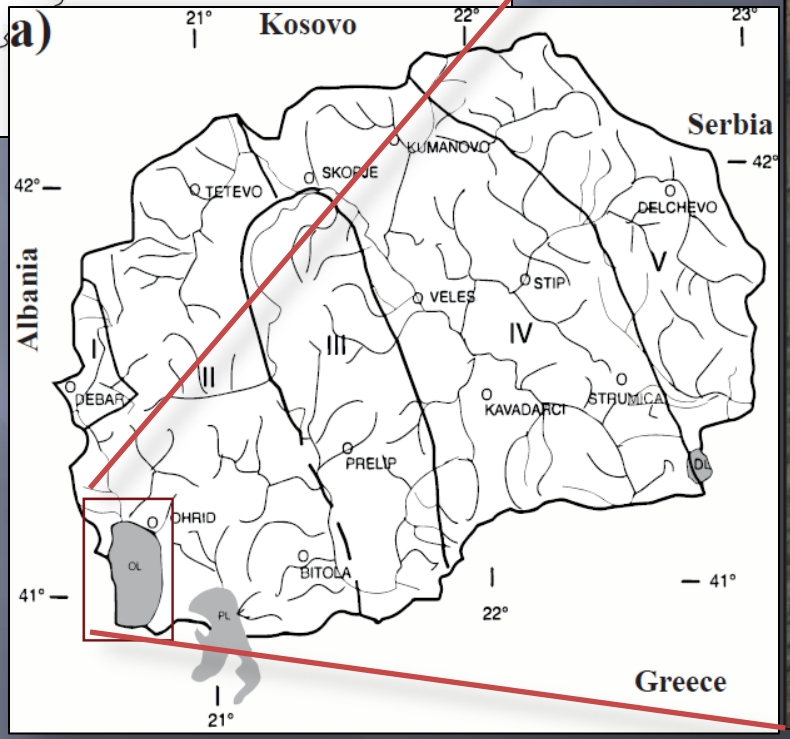
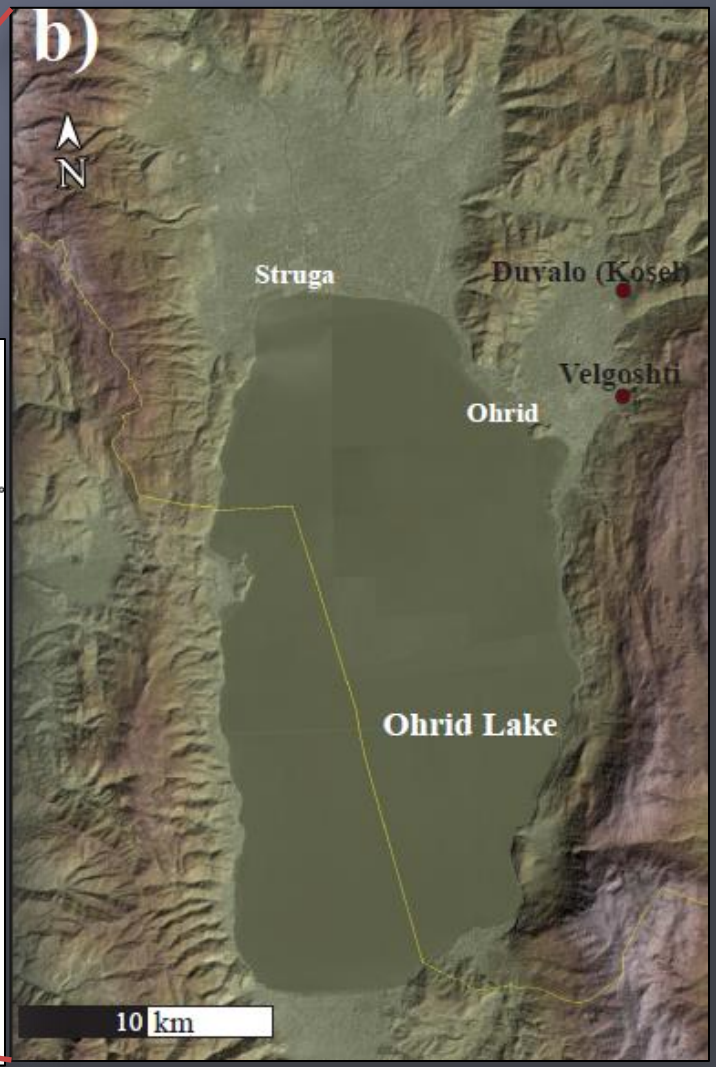
Isotope Climatology and Environmental Research Centre

Study area

Duvalo area is located close to the village of Kosel, in Ohrid region, in the South-western part of the Republic of North Macedonia .







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Study area

Duvalo
is characterized by a natural phenomenon of intense soil degassing.

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

Monument of nature DUVALO

The sulfur find "Duvalo" is an active post-volcanic phenomenon situated close to the village of Kosel, near Ohrid. Its appearance resembles miniature crater with a diameter of 0,5 m and depth of 30 cm. Gases of carbon dioxide and sulfur hydrogen are released from its hole, making this phenomenon mofeta (sulfur hydrogen find) and sulfatara (hole releasing gases of sulfur and hydrogen) at the same time. It represents the last trace of extinction of a former volcanic activity.

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But is it really a volcano?

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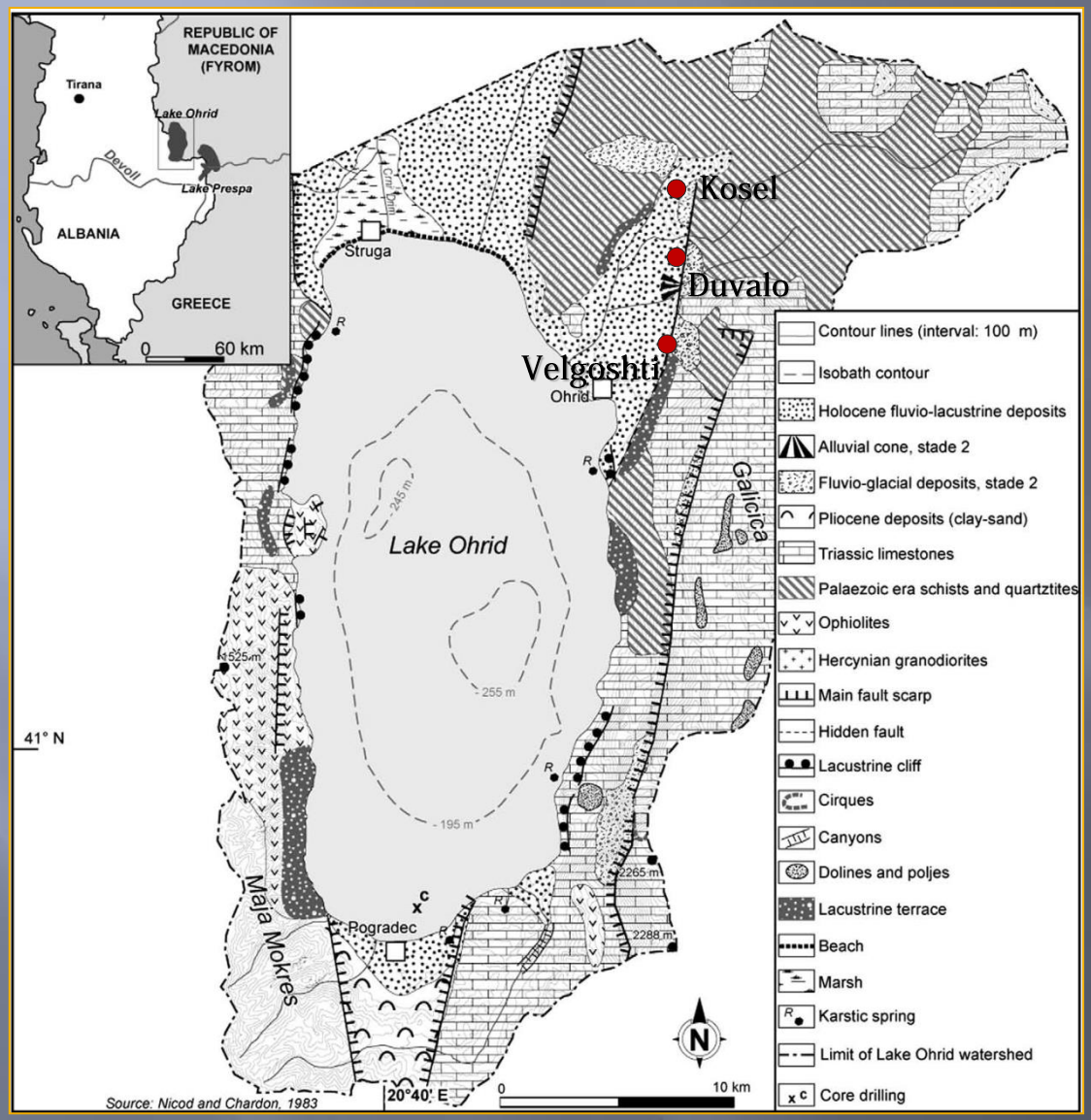
Geologic settings



L é zine et al., 2010

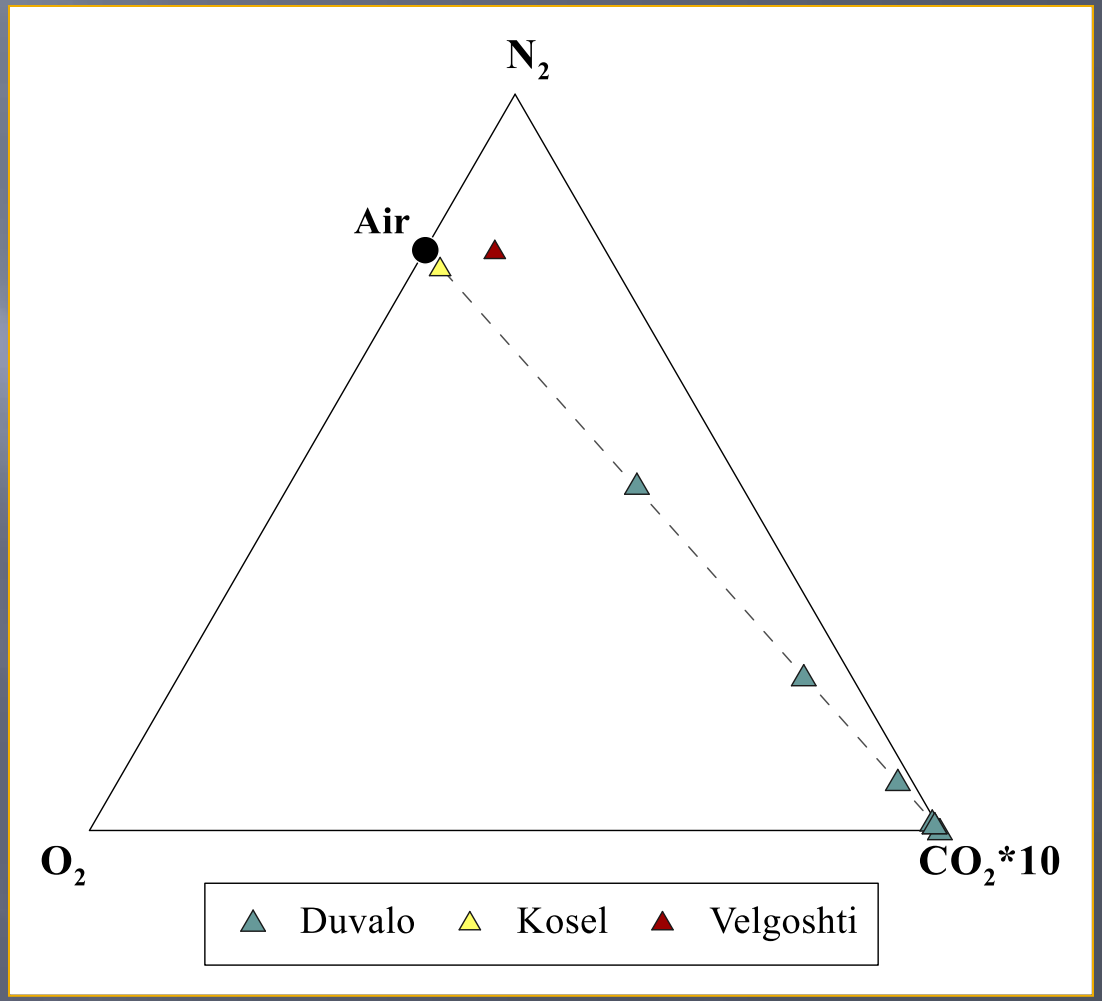
No volcanic rocks or volcanic activity has been documented in the geologic history of the Kosel area since Early Triassic (Markoski et al., 2018).

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).

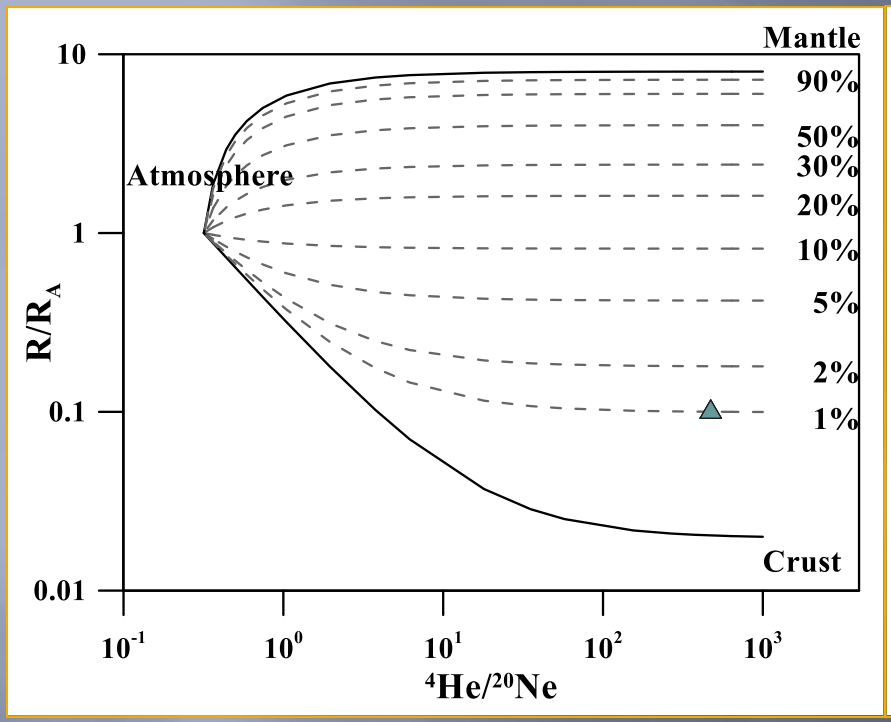
Chemical characterization

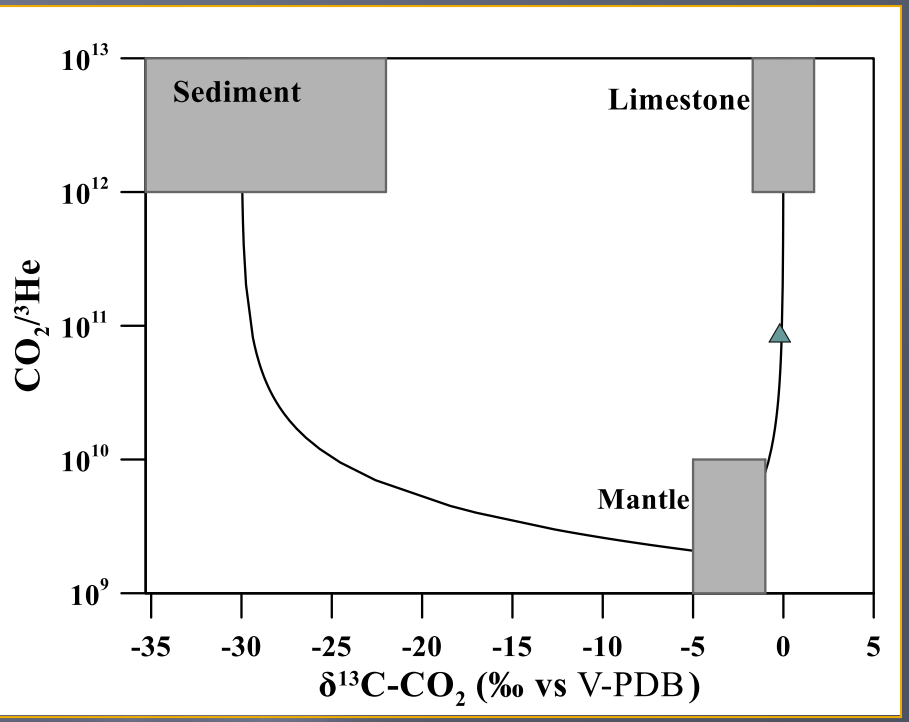
A mixing trend, typical of soil gases, between a CO_2-dominated end-member (CO_2 > 96%) of deep origin and the atmospheric air can be recognised.

Results of the samples richest in CO_2 are consistent with previous analyses (Trojanoviky, 1925; Iloski et al., 1957; Markovski et al., 2018), which reported that the gases were composed mainly of CO_2 (90-98%) and H_2S (0.8%).



Isotope characterization





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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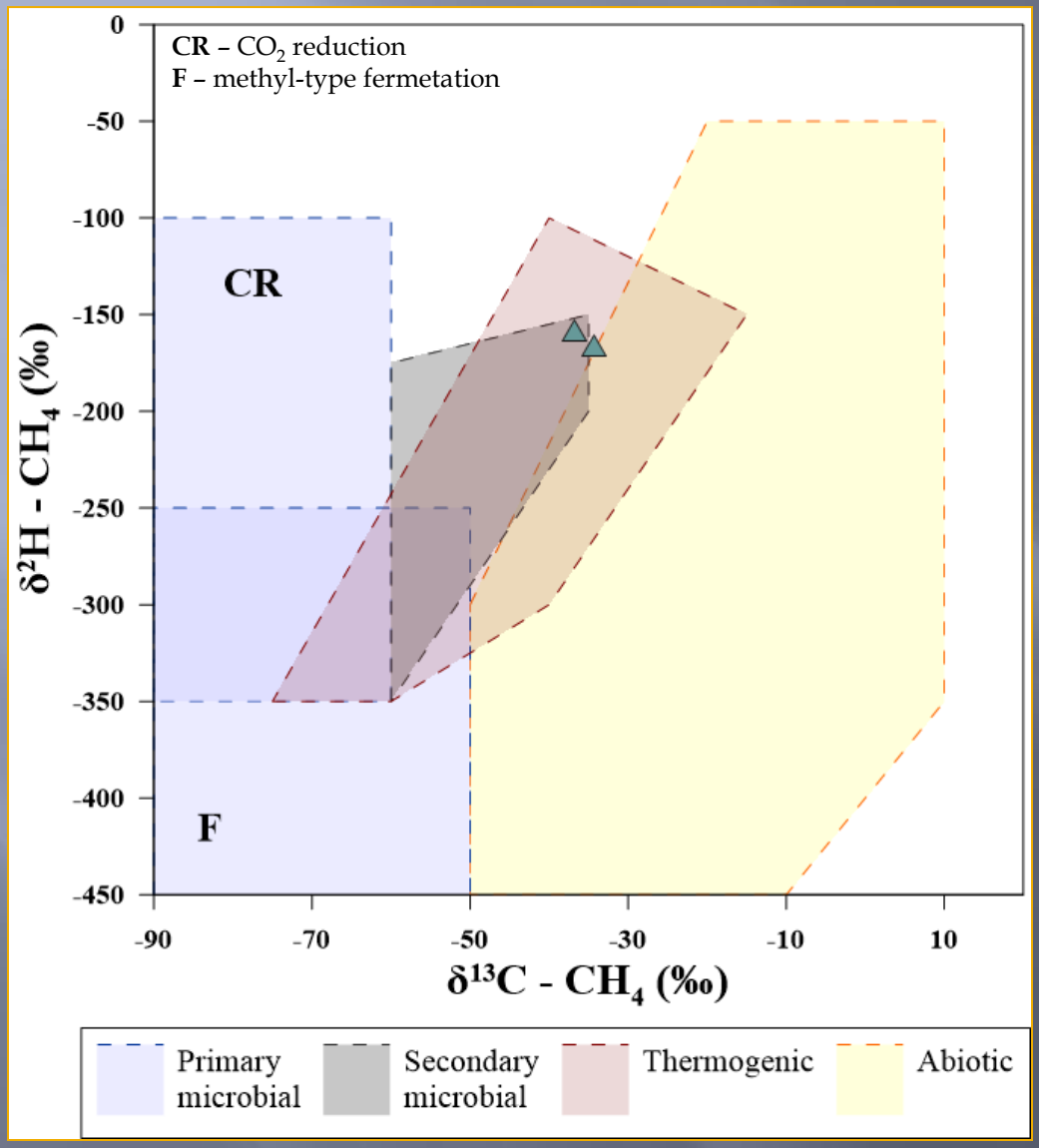
Isotope characterization — Methane



Isotope composition of methane shows:

- $\delta^{13}C$-CH_4 values range from -36.8 to -34.4 ‰ vs. V-PDB
- $\delta^{2}H$-CH_4 values vary between -166 and -158 ‰ vs. V-SMOW.

The samples fall within the thermogenic field.

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Sulfur origin

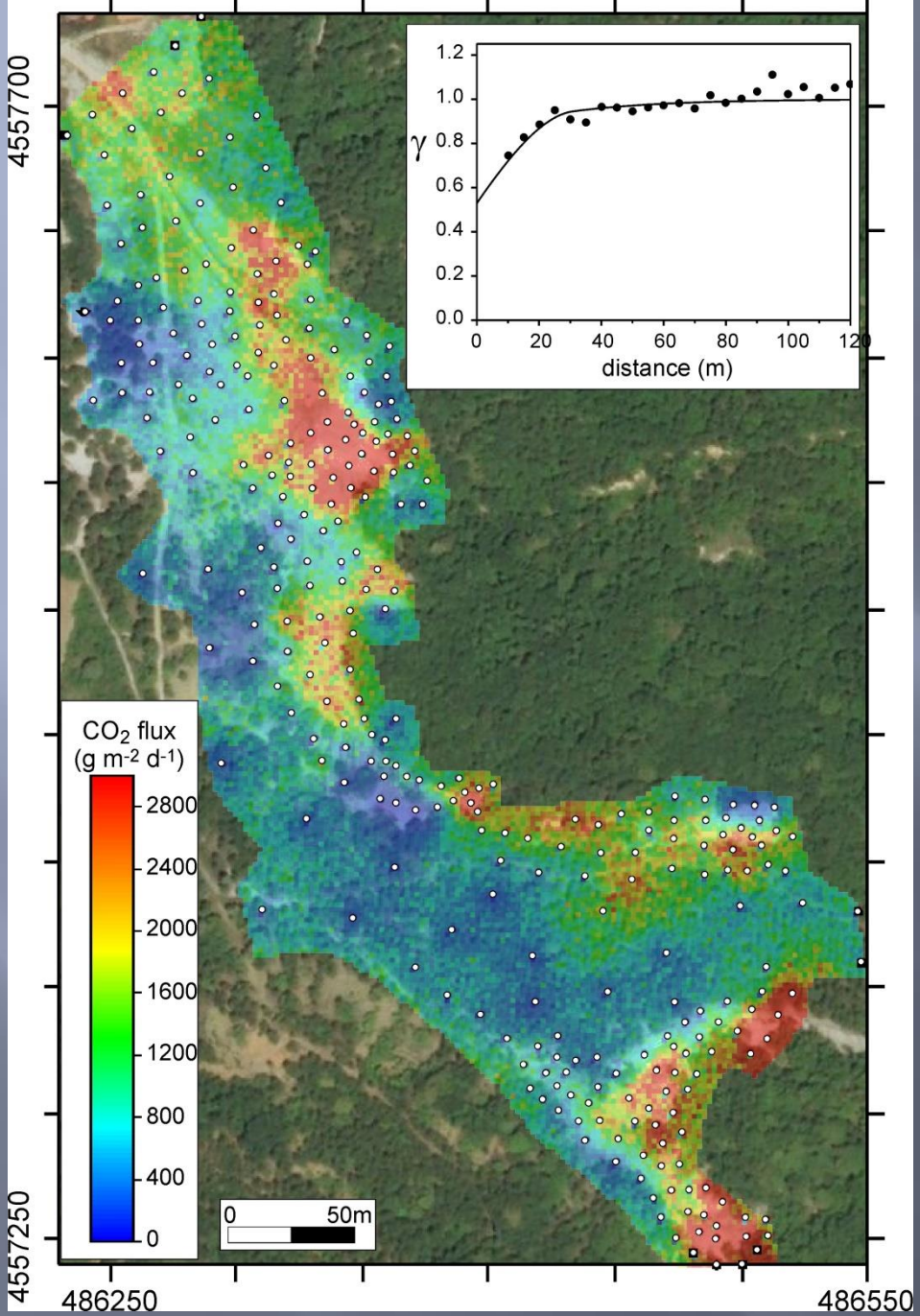
Hydrogen sulfide is found in the gases with concentrations up to 0.55%.
No sign of hydrothermal activity is present in the area. Therefore the most probable origin for H_2S is thermochemical sulfate reduction (TSR):

$$Hydrocarbons + CaSO_4 \rightarrow CaCO_3 + H_2S + H_2O \pm CO_2 \pm altered\ hydrocarbons \pm solid\ bitumen.$$

Part of the uprising H_2S is oxidized in the shallower part of the system and the produced sulphuric acid reacts with carbonate rocks producing abundant CO_2.

The enhanced permeability within the fault system of the area favours both TSR and H_2S oxidation processes and gas upflow to the surface.

Total CO_2 output estimation



Carbon dioxide flux measurements have been performed with the accumulation chamber method in Duvalo area.

Values up to 23,600 g/m^2/d have been measured

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

The total CO_2 output estimated for Duvalo site is **66.9 t/d**.

Conclusions

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.

Conclusions

The enhanced permeability deriving from tectonic activity favours the production at depth of H_2S 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 CO_2 that is degassed from the soils at Duvalo.

Such processes are so efficient to release to the atmosphere about 25,000 tons of CO_2 each year.