



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

Lorenza Li Vigni^{1,2}, Artur Ionescu^{3,4}, Kata Molnár⁵, Marjan Temovski⁵, László Palcsu⁵, Carlo Cardellini³, Antonina Lisa Gagliano¹, and Walter D'Alessandro¹

¹Istituto Nazionale di Geofisica e Vulcanologia, sezione di Palermo, Palermo, Italy (w.dalessandro@pa.ingv.it)

²Dipartimento di Scienze della Terra e del Mare, Università di Palermo, Italy (livignilorenza@gmail.com)

³Dipartimento di Fisica e Geologia, Università di Perugia, Italy (carlo.cardellini@unipg.it)

⁴Faculty of Environmental Science and Engineering, Babes-Bolyai University, Cluj-Napoca, Romania

(artur.ionescu@ubbcluj.ro)

⁵Isotope Climatology and Environmental Research Centre, Institute for Nuclear Research, Debrecen, Hungary

(temovski.marjan@atomki.mta.hu)

The Duvalo locality is located in the SW of the Republic of North Macedonia, in the Ohrid region, near the village of Kosel. It is an area of strong soil degassing, called “volcano” by the local people despite volcanic activity has never been documented in the recent geologic history of the area [1]. A large area (thousands of sqm) shows signs of strong alteration and is devoid of vegetation. Until the 19th century sulphur was mined from this area [1].

In August 2019, a campaign of soil CO₂ flux measurements and soil gas sampling was made. Duvalo is sometimes referred to as an active geothermal feature but no signs of enhanced geothermal gradient were found and the soil temperatures at 50 cm depth in this campaign were always within the range of local mean air temperatures. Soil CO₂ flux values ranged from 1.3 to 59,000 g/m²/d and can be modelled with the overlapping of 3 or 4 flux populations. A possible biological background is estimated in 6.8±1.8 g/m²/d while the other populations are characterized by an anomalous average flux ranging from 180 to 33,000 g/m²/d. The CO₂ total emission, estimated both with a statistical and geostatistical approach, provided similar values in the order of 50 t/d. This has to be considered as a minimum value because only areas with evident signs of alteration have been investigated. Nevertheless, the estimated output is quite high for an area unrelated with recent volcanism or geothermal activity.

The chemical composition of soil gases shows: CO₂ (96.6%), N₂ (1.8%), H₂S (0.6%) and CH₄ (0.3%) as the main gases. The present composition is almost indistinguishable from previous analyses made in 1957 and 1977 [1] pointing to a stability of the system in last decades. The isotope compositions indicate for CO₂ (δ¹³C -0.2 ‰) a pure carbonate rock origin, for CH₄ (δ¹³C -34.4 ‰ and δ²H -166 ‰) a thermogenic origin and for He (R/R_A 0.10) a pure crustal origin.

The H₂S released at Duvalo may be produced by either microbial or thermochemical sulphate reduction favoured by hydrocarbons whose presence can be inferred by the uprise of thermogenic methane. Partial oxidation of H₂S during its upflow, producing sulphuric acid, may be responsible of the production of abundant CO₂ through dissolution of carbonate rocks. Similar

processes have been evidenced also in other parts of North Macedonia [2]. These gases rise up through the N-S trending normal faults bordering the seismically active Ohrid basin graben [3] being released to the atmosphere through the soils of Duvalo “volcano”.

This research was funded by: DCO Grant n. 10881-TDB “Improving the estimation of tectonic carbon flux”; GINOP-2.3.2-15-2016-00009 ‘ICER’ project and PO-FSE Sicilia 2014–2020 (CUP: G77B17000200009).

References

[1] Markovski B. et al., 2018. Duvalo a geological phenomenon near Ohrid. DOI: 10.18509/AGB.2020.05

[2] Temovski M., 2017. Hypogene Karst in Macedonia. In: Klimchouk et al. (eds.), Hypogene Karst Regions and Caves of the World, Springer

[3] Hoffmann N. et al., 2010. Biogeosciences, 7, 3377–3386