



Gas Geochemistry and Fractionation Processes in Florina Basin, Greece

Kyriaki Daskalopoulou (1,2), Walter D'Alessandro (3), Sergio Calabrese (1,3), Carlo Cardellini (4), Antonina Lisa Gagliano (3), Artur Ionescu (5), Stylianos Karakatsanis (6), Konstantinos Kyriakopoulos (2), Lorenza Li Vigni (3), and Cristian Pop (5)

(1) Department of Earth and Marine Sciences, University of Palermo, Palermo, Italy, (2) Department of Geology and Geoenvironment, National and Kapodistrian University of Athens, Athens, Greece, (3) Istituto Nazionale di Geofisica e Vulcanologia, sez. Di Palermo, Palermo, Italy, (4) Department of Physics and Geology, University of Perugia, Perugia, Italy, (5) Faculty of Environmental Science and Engineering, Babeş-Bolyai University, Cluj-Napoca, Romania, (6) Department of Geology, Faculty of Sciences, Aristotle University of Thessaloniki, Thessaloniki, Greece

Florina Basin is located in northern Greece, close to Mount Voras where the volcanic activity of Late Messinian age began. In the area, many CO₂-rich gas emissions are present as a bubbling free-phase in groundwater (both springs and wells) and soil gases. Volcanism along with the geological and geodynamic regime of the basin, created the ideal conditions for CO₂ accumulation in vertically stacked reservoirs. One of these, industrially exploited by the company Air Liquide Greece, produces 30,000 t/a of CO₂. Results show that CO₂ concentrations in the gases of Florina can arrive up to 99.8% and are mostly above 90%. Moreover, C-isotope composition (-2.1 to + 0.3 ‰ vs. VPDB) indicates a mixed mantle-limestone origin for CO₂, while He isotope composition (R/R_A from 0.21 to 1.20) shows a prevailing crustal origin with an up to 15% mantle contribution. Helium and methane, with concentrations spanning over three orders of magnitude, show a positive correlation and a consequent high variability of He/CO₂ and CH₄/CO₂ ratios. This variability can be attributed to the interaction of the uprising gases with groundwater that chemically fractionates them due to their different solubility. Based on the CO₂, CH₄ and He concentrations, gas samples collected in the basin can be divided in 3 groups: a) deep reservoir gases, b) enriched in less soluble gases and c) depleted in less soluble gases. The first group consists of gas samples collected at the Air Liquide extraction wells, which tap a 300m deep reservoir. This group can be considered as the least affected by fractionation processes due to interaction with groundwater. The gases of the second group due to their interaction with shallower unsaturated aquifers, become progressively enriched in less soluble gases (He and CH₄). Finally, the third group represents residual gas phases after extensive degassing of the groundwater during its hydrological pathway.